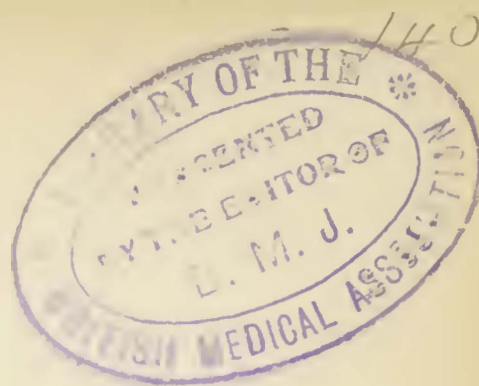


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THE PRINCIPLES OF CHEMISTRY

By D. MENDELÉEFF

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TRANSLATOR'S PREFACE

As in the previous English editions of these 'Principles,' so also in the present translation, it has been the aim of the Translator to give, as nearly as possible, a literal rendering of the Russian work.

All the more important of the new figures in the original have been reproduced, the only omissions, which are few in number, being either portraits or illustrations of well-known apparatus.

Of the Appendices issued with the first English edition, two have been retained; for permission to print the first of these we have to thank the Managers of the Royal Institution, while, for allowing the Faraday Lecture to appear, we are indebted to the Council of the Chemical Society of London. The matter of Appendix III. of the former English edition has now been incorporated into the text of the book, so that this appendix has been omitted. Its place is taken by an article, recently written by Professor Mendeléeff, on 'A Chemical Conception of the Ether.'

November, 1904.

G. K.
T. H. P.



AUTHOR'S PREFACE

TO

THE SEVENTH RUSSIAN EDITION

THIS work was written during the years 1868–1870, its object being to acquaint the student not only with the experimental facts and laws of chemistry, but also with the insight given by this science into the unchangeable substratum underlying the varying forms of matter.

If statements of fact themselves depend upon the person who observes them, how much more distinct is the reflection of the personality of him who gives an account of methods and philosophical speculations forming the essence of a science! For this reason there will inevitably be much that is subjective—bearing the stamp of time and locality—in every objective exposition of science. And as an individual production is only significant in virtue of that which has preceded and that which is contemporary with it, it resembles a mirror, which in reflecting exaggerates the size and clearness of neighbouring objects, and causes a person near it to see reflected most plainly those objects which are on the side to which it is directed, and sometimes even the person holding the mirror. Although I have endeavoured to make my book a true mirror directed towards the whole domain of chemical changes and of the elements taking part in them, yet involuntarily those influences near to me being the most clearly reflected and the most brightly illuminated have tinted the entire work with their colouring. In this way the chief peculiarity of the book has

been determined. Experimental and practical data and their application in life and industry occupy their place, but the philosophical principles of our science form the chief theme of the work. In former times sciences, like bridges, could only be built up by supporting them on a few broad buttresses and long girders. In addition to the exposition of the principles of chemistry, it has been my desire to show how this science has now been built up like a suspension bridge, supported by the united strength of a number of slender, but firmly fixed, chains—individually of little strength—and has thus been carried over difficulties which before appeared insuperable. In comparing the science of the past, the present, and the future, in placing the particulars of its restricted experiments side by side with its aspirations after unbounded and infinite truth, and in restraining myself from yielding to a bias towards the most attractive path, I have endeavoured to incite in the reader a spirit of inquiry which, dissatisfied with speculative reasonings alone, should subject every idea to experiment, to encourage the habit of stubborn work, and to excite a search for fresh chains of evidence to complete the bridge over the bottomless unknown. History proves that it is possible by this means to avoid three equally pernicious extremes: the Utopian—a visionary contemplation which strives to create all from an impulse of thought alone—the stagnant realism which is content with bare facts, and presumptuous scepticism, irresolute about everything. Sciences like chemistry, which deal with ideas as well as with material substances, and create a possibility of immediately verifying that which has been or may be discovered or assumed, demonstrate at every step that the work of the past has availed much, and that, without it, it would be impossible to advance into the ocean of the unknown. They also show the possibility of becoming acquainted with fresh portions of this unknown, and compel us, while duly respecting the teachings of history, to cast aside classical illusions, and to engage in the work of tranquil and systematic investigation,

which is not only the sole means of attaining mental satisfaction, but is also practically useful to ourselves and all our fellow-creatures.¹

¹ Chemistry, like every other science, is at once a means and an end. It is a means of attaining certain practical results. Thus, by its assistance, the obtaining of matter in its various forms is facilitated; it shows new possibilities of availing ourselves of the forces of nature, indicates the methods of preparing many substances, points out their properties, &c. In this sense chemistry is closely connected with the work of the manufacturer and the artisan, it plays a useful part, and is a means of promoting the general welfare. Besides this honourable vocation, chemistry has another. With it, as with every other elaborated science, there are many lofty aspirations, the contemplation of which serves to inspire its workers and adherents. This contemplation comprises not only the principal data of the science, but also the generally accepted deductions, together with hypotheses which refer to phenomena as yet but imperfectly known. In this latter sense scientific contemplation varies much with times and persons, it bears the stamp of creative power, and embraces the highest forms of scientific progress. In that pure enjoyment experienced on approaching to the ideal, in the eagerness to draw aside the veil from the hidden truth, and even in that discord which exists between the various workers, we ought to see the surest pledges of further scientific progress. Science thus advances, discovering new truths, and at the same time obtaining practical results. The edifice of science not only requires material, but also a plan, and necessitates the work of preparing the materials, putting them together, working out the plans and the symmetrical proportions of the various parts. To conceive, understand, and grasp the whole symmetry of the scientific edifice, including its unfinished portions, is equivalent to tasting that enjoyment only conveyed by the highest forms of beauty and truth. Without the material, the plan alone is but a castle in the air, a mere possibility; whilst the material without a plan is but useless matter. All depends on the concordance of the materials with the plan and execution, and the general harmony thereby attained. In the work of science the artisan, architect, and creator are very often one and the same individual; but sometimes, as in other walks of life, there is a difference between them; sometimes the plan is preconceived, sometimes it follows the preparation and accumulation of the raw material. Free access to the edifice of science is not only allowed to those who devised the plan, worked out the detailed drawings, prepared the materials, or piled up the brickwork, but also to all those who are desirous of making a close acquaintance with the plan, and wish to avoid dwelling in the vaults or in the garrets where the useless lumber is stored.

Knowing how contented, free, and joyous is life in the realm of science, one fervently wishes that many would enter its portals. On this account many pages of this treatise are unwittingly stamped with the earnest desire that the habits of chemical contemplation which I have endeavoured to instil into the minds of my readers will incite them to the further study of science. Science will then flourish in them and by them, on a fuller acquaintance not only with that little which is enclosed within the narrow limits of my work, but with the further learning which they must imbibe in order to make themselves masters of our science and partakers in its further advancement.

Those who enlist in the cause of science have no reason to fear when they remember the urgent need for practical workers in the spheres of agriculture, arts,

Thus the desire to direct those thirsting for truth to the pure source of the science of the forces acting throughout nature forms the first and most important aim of this book. The time has arrived when a knowledge of physics and chemistry forms as important a part of education as that of the classics did two centuries ago. In those days the nations which excelled in classical learning stood foremost, just as now the most advanced are those which are superior in the knowledge of the natural sciences, for they represent the strength as well as the signs of our times. If the universe clearly exhibits a unity of purpose, the cause of this is surely first seen in the unity of the principles of science, which inevitably become more and more uniform and progressive, and, although individually untrammelled, are bound to submit to the yoke of laws conceived and revealed. And chemistry, as the youngest branch of natural science, promises in the future a richer harvest than it has already given. One of the chief aims of this book is to attract and retain fresh, unshackled forces for this youthful science by pointing out what has been achieved, what remains to be achieved, and in what directions advances may be made. Only by gradually extending the conquests already made can the coming generation of chemists benefit mankind and disperse the shades of ignorance and superstition. The seeds sown by science are reaped by mankind. In contemplating the infinite, science has no limits.

Although I feel confident that 'good will' will be awakened by our science, I know that time is long, and that many efforts, conditions, and circumstances are needed for the fruits to ripen.

While following the above and chief aim, I set myself also a second object: to furnish a text-book giving an elementary knowledge of chemistry, and so satisfy a want which undoubtedly exists among students and those who have recourse

and manufacture. By summoning adherents to the work of theoretical chemistry, I am confident that I call them to a most useful labour, to the habit of dealing correctly with nature and its laws, and to the possibility of becoming truly practical men.

to chemistry either as a source of truth or as a means of living.² Hence, although the fundamental object of this work was to express and embrace the general chemical teaching of the present day from a personal point of view, I have nevertheless striven throughout to maintain such a level as would render the 'Principles of Chemistry' accessible to the beginner.

² I recommend those who are commencing the study of chemistry with my book *to first read only what is printed in large type*, because in that part I have endeavoured to concentrate all the fundamental, indispensable knowledge required for that study. In the footnotes, printed in small type (which should be read only after the large text has been mastered), certain details are discussed; they are either further examples, or debatable questions on existing ideas which I thought useful to lay before those entering into the sphere of science, or certain historical and technical details which might be withdrawn from the fundamental portion of the book. Without intending to attain in my treatise to the completeness of a work of reference, I have still endeavoured to express the principal developments of science as they concern the chemical elements viewed in that aspect in which they appeared to me after long-continued study of the subject and participation in the contemporary advance of knowledge.

I have also placed my personal views, suppositions, and arguments in the footnotes, which are chiefly designed for details and references. But I have endeavoured to avoid here, as in the text, not only all that I consider doubtful, but also those details which belong either to special branches of chemistry (for instance, to analytical, organic, physical, theoretical, physiological, agricultural, or technical chemistry) or to different branches of natural science which are gradually coming into closer and closer contact with chemistry. Chemistry, I am convinced, must occupy a place among the natural sciences side by side with mechanics; for mechanics treats of matter as a system of ponderable points having scarcely any individuality and only standing in a certain state of mobile equilibrium. For chemistry, matter is an entire world of life, with an infinite variety of individuality both in the elements and in their combinations. In studying the general uniformity from a mechanical point of view, I think that the highest point in the knowledge of nature cannot be attained without taking into account the individuality of things in which chemistry is set to seek for general higher laws. Mechanics forms the classical basis of natural philosophy, while chemistry, as a comparatively new and still young science, already strives to—and will, in the future—introduce a new, living aspect into the philosophy of nature; all the more is this so, as chemistry alone is never at rest or anywhere dead—its vital action has universal sway, and inevitably determines the general aspect of the universe. Just as the microscope and telescope enlarge the scope of vision, and discover life in seeming immobility, so chemistry, in discovering and striving to discern the life of the invisible world of atoms and molecules and their ultimate limit of divisibility, will clearly introduce new and important problems into our conception of nature. And I think that its *rôle*, which is now considerable, will increase more and more in the future; that is, I think that, in its further development, it will occupy a place side by side with mechanics for the comprehension of the secrets of nature. But here we require some second Newton; and I have no doubt but that he will soon appear.

Many aspects of this work are determined by this combination of requirements, which frequently differ widely. In the preparation of such a book it is necessary not to be carried away by what appears to be a plausible theory in explaining individual facts and to always endeavour to transmit the simple truth of a given fact, extracting it from the vast store of the literature of the subject and from tried personal experience. In publishing a new edition of this work I have striven to add any facts of importance recently discovered and to revise the former edition in the above spirit. With this object I have gone entirely over this edition, and a comparison of it with the former one will show that the additions and alterations have, in many instances, cost as much labour as their original compilation. I also wished to show in an elementary treatise on chemistry the striking advantages gained by the application of the periodic law, which I first saw in its entirety in the year 1869, when I was engaged in writing the first edition of this book, in which, indeed, the law was first enunciated. At that time, however, this law was not established so firmly as now, when so many of its consequences have been verified by the researches of numerous chemists. The, to me, unexpectedly rapid success with which the teaching of the periodicity of the elements has spread in our science, and perhaps, also, the perseverance with which I collected in this work, and upon a new plan, the most important data respecting the elements and their mutual relations, explained sufficiently the fact that the former editions of my work have been translated into English³ and German.⁴ Deeply touched by the favourable opinions expressed by English and American men of science upon my book, I ascribe them chiefly to the periodic law placed at the basis of my treatise, and especially of the second part of the book, which contains a large amount of data having a special, and sometimes unex-

³ The English translation was made by G. Kamensky, and edited by A. J. Greenaway; published by Longmans, Green & Co.

⁴ The German translation was made by L. Jawein and A. Thillot; published by Ricker (St. Petersburg).

pected, bearing from the point of view of this law. As the entire scheme of this work is subordinated to the law of periodicity, which may be illustrated in a tabular form by placing the elements in series, groups, and periods, such tables are given at the end of this Preface.

But the thought that this book might fall not only into the hands of the beginner for whom it is intended, but also of authorities who might wish to know the views held by an old disciple of science on the current problems of chemistry, greatly complicated the preparation of a new edition, for it necessitated making a selection of the most essential of the vast number of new researches published year by year, and explaining my views on them without greatly enlarging the bulk of the work.⁵ After having closely followed all the chief conquests of chemical science since the days of Berzelius, Liebig, Dumas, and Gerhardt, and having seen the triumph of much that lay neglected and the fall of much that was exalted, I involuntarily acquired a tendency to analyse new facts and a desire to transmit to my readers the results of such analysis, if it could, in my opinion, help towards a proper explanation and generalisation of the chemical elements. In carefully preparing this

⁵ A mere dry and impersonal statement of facts and of the opinions of others, although new and important, would in no way correspond with the spirit of this book, which is mainly designed for the beginner, and for the expression of my personal views on the chemical elements. In my opinion, only a connection of ideas with facts, and of observations with a line of thought, can act in the right direction; otherwise reality slips away and fiction easily supersedes it, as has been, is, and will be frequently the case, and this I strenuously wish to avoid in this book. My chief desire is to inspire a spirit of inquiry, and if I often express my personal opinions, I do not wish to hide either the reasons which guide others in another direction or views which are contrary to my own. Of these views I may mention those which recognise an 'electrolytic dissociation' in saline solutions, the formation of the chemical elements from a single primary matter, &c. In shortly, but as far as possible exactly and objectively, stating observed facts, I endeavour, as well as I am able, to elucidate their sense and to group them in a precise and real manner, revealing further horizons for future scientific research. I have tried to exclude nothing which I knew and considered reliable and instructive, although it might have contradicted my views. Notwithstanding the care I have taken in collecting the difficult data cited in this book, I am far from thinking that it contains a complete review of all that is instructive in the doctrine of the chemical elements.

edition, I have not lost sight of the fact that I am hardly likely to publish another, and I have therefore, in many cases, spoken more definitely than formerly. After having been an insignificant but zealous worker in chemistry for almost half a century, I wished that my book should retain some traces of how a confirmed disciple of Gerhardt regards the fundamental problems of the theory of the chemical elements at the beginning of the twentieth century. As an example, I may mention that the more I have thought on the nature of the chemical elements, the more decidedly have I turned away from the classical notion of a primary matter, and from the hope of attaining the desired end by a study of electrical and optical phenomena, and the more clearly have I recognised that first and foremost are needed truer conceptions of 'mass' and 'ether' than those in vogue at the present time.⁶ The return to electro-chemism

⁶ When I consider the undoubtedly real and all-permeating 'ether,' and involuntarily ask myself of what it consists, I cannot admit the idea that its atoms or matter are only composed of a 'primary matter' of which all atoms are built up, for if that were so one might expect not only cases of the appearance and disappearance of the 'mass' of a substance, but also of the transformation of one element into another, and all we know forces us to deny that this is possible, although thousands—from the spiritualists to Emmens (the conversion of silver into gold, 1897) and Fittica (the conversion of phosphorus into arsenic, 1900)—have tried and are trying to prove the contrary. And, of course, no one except a metaphysician would permit himself, and will hardly ever consent, to deny the presence of matter, 'atoms,' and mass in 'ether.' And if we recognise the materiality and mass of 'ether,' it seems to me first of all necessary to admit that it is a substance without power of chemical reaction on other substances. Not so long ago such an idea might have appeared most unreal; but now, when instances of substances incapable of reacting have been discovered in argon and its analogues, this view is quite possible. Besides being admissible, a light substance deprived of all chemical force should apparently certainly exist and is to be foreseen. Moreover, the distribution of the elements according to groups and series (Preface, tables I. and II.) in the periodic system, and the fact that a zero group must be recognised besides groups I.–VIII., give reason for thinking that there is also a zero series of elements lighter than hydrogen, and even an element in the hydrogen series of the zero group (is not this coronium or one of the volcanic gases, the spectra of which were observed by Nasini, Anderlini, and Salvadori in 1898?), and an element of the zero series and zero group should be many times lighter than hydrogen in its atomic weight. Let us call this weight x . It should be an unliquefiable gas, and its density with respect to hydrogen under like conditions should be $x/2$, i.e. its molecule should contain one atom like that of helium, argon, &c. The extremely small density of the gas, i.e. the extremely rapid motion proper to its molecules, their very small weight, and also the position in the zero

which is so evident in the supporters of the hypothesis of 'electrolytic dissociation,' and the notion of a splitting up of atoms into 'electrons,' in my opinion only complicate and in no way explain so real a matter (since the days of Lavoisier) as the chemical changes of substances, which led to the recognition of the invariable and ponderable atoms of simple bodies. The definition of mass gave a means for analysing and grasping chemical transformations of substances, and for arriving at the atom, while the mass of the atom was shown by the periodic law to influence all its chief chemical properties. Thus chemistry in its principles stood on the firm foundations laid by Galileo, Newton, and Lavoisier, and in order to gain further insight and knowledge of the atoms themselves, the fundamental conceptions of mass, gravity, and ether will have to be explained by a method of experiment alone, otherwise the realism of science will again open its doors to such metaphysical and 'metachemical' conceptions as phlogiston and other mystical dreams. For my part, I endeavour to remain true to the testament of realism left by Newton and Lavoisier, and it is my wish to instil this sentiment into my young readers.

In this seventh edition I have not found it necessary to alter any of the essential features of previous editions, and have only completed them by the addition of many new details. In this respect invaluable assistance has been rendered me by my dear friend, Professor Brauner, of the University of Prague, by his complete and concise contribution on the 'Elements of the Rare Earths,' which he wrote at my request. Many data have been added thereto in recent years, and it needs such an authority on the 'rare earths' as Professor Brauner to interpret this complex, difficult, and yet unfinished subject, where the obtaining

group, should contribute to the fact that this gas should permeate and penetrate everywhere; that it should occupy space, but not attach itself stably to anything with the harmonious motion of chemical combination, so that it cannot accumulate anywhere. And these imaginary properties should also be those of the substance 'ether.' In endeavouring to clothe the conception of 'ether' with a chemical dress, and so render it an actual, real possibility in harmony with the purely realistic periodic law, I think I am serving the cause of unity in natural philosophy.

of reliable data is complicated not only by the peculiarities and analogies of many facts, but also by the rareness of the earths themselves. Professor Brauner has himself contributed largely to the history of these metals, and his description of them contains much of his individual work. I offer him my most grateful thanks for his contribution. I am also greatly indebted to Mr. V. D. Saposhnikoff for revising the sheets for the press and for compiling the Index, which will be found of great help to those seeking for any special subject in this book.

D. MENDELÉEFF.

ST. PETERSBURG : *November 27, 1902.*

THE PERIODS OF THE CHEMICAL ELEMENTS, TAKING THE ATOMIC WEIGHT OF O = 16.

			Higher saline oxides.	Groups.	Elements of even series.					
Gaseous hydrogen compounds.	Higher saline oxides.	Groups.	R ₂ O	I	K=39.1	Rb= 85.4	Cs=132.9	—	—	
			RO	II	Ca=40.1	Sr= 87.6	Ba=137.4	—	Rd= 224.7	
			R ₂ O ₃	III	Sc=44.1	Y= 89.0	La=139	Yb=173	—	
			RO ₂	IV	Ti=48.1	Zr= 90.6	Ce=140 ⁶	—	Th=232	
			R ₂ O ₅	V	V=51.4	Nb= 94.0	—	Ta=183	—	
			RO ₃	VI	Cr=52.1	Mo= 96.0	—	W=184	U=239	
			R ₂ O ₇	VII	Mn=55.0	?= 99 ¹	—	—	—	
			VIII	{	Fe=55.9	Ru=101.7	—	Os=191	—	
					Co=59	Rh=103.0	—	Ir=193	—	
					Ni=59 ³	Pd=106.5	—	Pt=194.9	—	
Typical elements.										
R ₂ O	I	H=1.008	Li= 7.03	Na=23.05	Cu=63.6	Ag=107.9	—	Au=197.2		
RO	II		Be= 9.1	Mg=24.3	Zn=65.4	Cd=112.4	—	Hg=200.0		
R ₂ O ₃	III		B=11.0	Al=27.0	Ga=70.0	In=114.0	—	Tl=204.1		
RH ₄	RO ₂	IV	C=12.0	Si=28.4	Ge=72.3	Sn=119.0	—	Pb=206.9		
RH ₃	R ₂ O ₅	V	N=14.04	P=31.0	As=75.0	Sb=120.0	—	Bi=208		
RH ₂	RO ₃	VI	O=16.00	S=32.06	Se=79	Te=127 ⁵	—	—		
RH	R ₂ O ₇	VII	F=19.0	Cl=35.45	Br=79.95	I=127	—	—		
0	0	0 ¹	He=4.0	Ne=19.9	Ar=38 ²	Kr=81.8	Xe=128	—		
					Elements of uneven series.					

D. MENDELÉEFF.
1869-1902.

¹ The atomic weights of helium, argon, and the analogous gases, judging from their densities (pp. 247-253), are greater than those of the halogens and less than those of the metals of the alkalies, but no compounds of these elements are known.

² The density of argon indicates an atomic weight 39.9; but, judging from the preceding note, it is probably greater than that of Cl but less than that of K, i.e. about 38.

³ The atomic weight of Ni is given as 58.7; but as this metal, judging from its properties, should follow after Co = 59, its atomic weight should not be less but greater than that of Co. Therefore it is probable that further research will prove these atomic weights to be slightly different from the above.

⁴ The discovery of a metal resembling Mn (ekamanganese) with an atomic weight 99 may be expected.

⁵ Judging by its properties and the periodic law, tellurium should have an atomic weight less than that of iodine, but so far experiment proves the contrary—the values obtained for Te varying from 126.4 (Steiner) to 127.9 (Metzner) with an average of 127.7, that of iodine being slightly less—126.96 (Stas), and 126.98 (Ladenburg). Both these latter figures are near 127, and it is therefore likely that further research will prove that the atomic weight of iodine is greater than 127 (which is possible because the iodine was dried with CaCl₂, which might introduce chlorine), or else a figure smaller than 127 may be afterwards found for tellurium.

⁶ A whole large period is wanting between Ce = 140 and Ta = 183, but the series of rare elements (they have not been fully investigated)—for instance, Pr = 140.5, Nd = 143.6, Gd = 156, Er = 166, Yb = 173, &c.—have, as far as is now known, atomic weights which exactly fill this interval, and therefore this portion of the periodic system is, in a way, broken and requires fresh researches.

⁷ According to Madame Curie (1902), *radium* (Vol. II., p. 328) (one of the radio-active elements) resembles barium and has an atomic weight lying between 223 and 225.

PERIODIC SYSTEM OF THE ELEMENTS IN GROUPS AND SERIES.

Series	GROUPS OF ELEMENTS										
	O	I	II	III	IV	V	VI	VII	VIII		
1	—	Hydrogen H 1·008	—	—	—	—	—	—			
2	Helium He 4·0	Lithium Li 7·03	Beryllium Be 9·1	Boron B 11·0	Carbon C 12·0	Nitrogen N 14·04	Oxygen O 16·00	Fluorine F 19·0			
3	Neon Ne 19·9	Sodium Na 23·05	Magnesium Mg 24·3	Aluminium Al 27·0	Silicon Si 28·4	Phosphorus P 31·0	Sulphur S 32·06	Chlorine Cl 35·45			
4	Argon Ar 38	Potassium K 39·1	Calcium Ca 40·1	Scandium Sc 44·1	Titanium Ti 48·1	Vanadium V 51·4	Chromium Cr 52·1	Manganese Mn 55·0	Iron Fe 55·9		
5		Copper Cu 63·6	Zinc Zn 65·4	Gallium Ga 70·0	Germanium Ge 72·3	Arsenic As 75	Selenium Se 79	Bromine Br 79·95	Cobalt Co 59		
6	Krypton Kr 81·8	Rubidium Rb 85·4	Strontium Sr 87·6	Yttrium Y 89·0	Zirconium Zr 90·6	Niobium Nb 94·0	Molybdenum Mo 96·0		Nickel Ni 59		
7		Silver Ag 107·9	Cadmium Cd 112·4	Indium In 114·0	Tin Sn 119·0	Antimony Sb 120·0	Tellurium Te 127	Iodine I 127	Ruthenium Ru 101·7		
8	Xenon Xe 128	Cæsium Cs 132·9	Barium Ba 137·4	Lanthanum La 139	Cerium Ce 140	—	—	—	—		
9		—	—	—	—	—	—	—	—		
10	—	—	—	Ytterbium Yb 173	—	Tantalum Ta 183	Tungsten W 184	—	Platinum Pt 194·9		
11		Gold Au 197·2	Mercury Hg 200·0	Thallium Tl 204·1	Lead Pb 206·9	Bismuth Bi 208	—	—	Iridium Ir 193		
12	—	—	Radium Rd 224	—	Thorium Th 232	—	Uranium U 239		Osmium Os 191		
HIGHER SALINE OXIDES											
R R ₂ O RO R ₂ O ₃ RO ₂ R ₂ O ₅ RO ₃ R ₂ O ₇ RO ₄											
HIGHER GASEOUS HYDROGEN COMPOUNDS											
RH ₄ RH ₃ RH ₂ RH											

INTRODUCTION

THE rapid development of the study ¹ of the external universe, dating from the days of Galileo (†1642) and Newton (†1727), led to the

¹ The investigation of a substance or a natural phenomenon consists: (*a*) in determining the relation of the object under examination to that which is already known, either from previous researches, or from experiment, or from the knowledge of the common surroundings of life—that is, in determining and expressing the quality of the unknown by the aid of that which is known; (*b*) in measuring all that which can be subjected to measurement, and thereby indicating the quantitative relation of that under investigation to that already known—to time and space, temperature, mass, &c.; (*c*) in determining the position held by the object under investigation in the system of known objects, taking into account both qualitative and quantitative data; (*d*) in determining, from the quantities which have been measured, the empirical (visible) dependence (function, or ‘law,’ as it is sometimes termed) of variable factors—for instance, the dependence of the composition of a substance on its properties, of temperature on time, of properties on mass (weight), &c.; (*e*) in framing hypotheses or suppositions as to the actual cause and nature of the relation of that studied to that which is known or to the categories of time, space, &c.; (*f*) in experimentally verifying the logical consequences of such hypotheses; and (*g*) in advancing a theory which shall account for the nature of the properties of that studied in its relations with things already known and with the conditions under which it exists. It is manifest that it is only possible to carry out these investigations when we have taken as a basis something which is incontestable and self-evident to our understanding; such, for instance, as number, time, space, matter, form, motion, or mass. Hence it follows that in the investigation of anything, there always remains something which is accepted without investigation, or admitted as a known and recognised factor; the axioms of geometry may be taken as an example. Thus in the science of biology it is necessary to admit the faculty of organisms for multiplying themselves, as a conception whose meaning is as yet unknown. In the study of chemistry, too, the notion of elements must be accepted almost without any further analysis. However, by investigating and describing what is visible and open to direct observation by the organs of the senses, we may hope to arrive, first at hypotheses, and afterwards at theories, of what has now to be taken as the basis of our investigations. The minds of the ancients strove to seize at once the very fundamental categories of investigation, whilst all the successes of recent knowledge are based on the above-cited method of investigation, without the determination of ‘the beginning of all beginnings.’ By following this inductive method, the *exact sciences* have already succeeded in becoming accurately acquainted with much of the invisible world, not directly perceptible to the organs of sense (for example, the molecular motion of all bodies, the composition of the heavenly luminaries, and the paths of their motion, the necessity for the existence

separation of Chemistry as a special branch of natural philosophy. Not only was this owing to the increasing store of observations and experiments relating to the transformations of substances, but more especially because, in addition to gravity, cohesion, heat, light, and electricity, it became necessary to recognise the existence of peculiar internal forces in the ultimate parts of all substances, forces which make themselves manifest in the transformations of substances into one another, but remain hidden (latent) under ordinary circumstances, and whose existence cannot therefore be directly apprehended, and so for a long time remained unrecognised. The primary object of chemistry is the study of the homogeneous substances ² of which all the objects of the universe

of substances as yet unknown to experiment, &c.), and have verified the knowledge thus obtained, and employed it for increasing the interests of humanity. It may therefore be safely said that *the inductive method of investigation* is a more perfect mode of acquiring knowledge than the deductive method alone (which from a little of the unknown accepted as incontestable arrives at much which is visible and observable) by which the ancients strove to embrace the universe. By investigating the universe by an inductive method (endeavouring from the much which is observable to arrive at a little which may be verified and is indubitable), the new science refuses to recognise dogma as *truth*, but through *reason*, by a slow and laborious method of investigation, strives for and attains to true deductions.

² Substance or matter is that which occupies space and has weight; that is, which presents a mass attracted by the earth and by other masses of matter, and of which the *objects* of nature are composed, and by means of which the motions and *phenomena* of nature are accomplished. It is easy to discover, by examining and investigating in various ways the objects met with in nature and in the arts, that some of these are homogeneous, whilst others are composed of a mixture of several homogeneous substances. This is most clearly apparent in solid substances. The metals used in the arts (for example, gold, iron, copper) must be homogeneous, otherwise they are brittle and unfit for many purposes. Homogeneous matter exhibits similar properties in all its parts. By breaking up a homogeneous substance we obtain parts which, although different in form, resemble each other in their properties. Glass, pure sugar, marble, salt, &c., are examples of homogeneous substances. Examples of non-homogeneous substances are, however, much more frequent in nature and the arts. Thus the majority of the rocks are not homogeneous. In porphyries bright pieces of a mineral called 'orthoclase' are often seen interspersed amongst the dark mass of the rock. In ordinary red granite it is easy to distinguish large pieces of orthoclase mixed with dark semi-transparent quartz and flexible laminæ of mica. Similarly, plants and animals are non-homogeneous. Thus, leaves are composed of skin, fibre, pulp, sap, a green colouring matter, &c. As an example of non-homogeneous substances artificially produced, gunpowder may be cited, which is prepared by mixing together sulphur, nitre, and charcoal. Many liquids, also, are not homogeneous, as may be observed by the aid of the microscope, when drops of blood are seen to consist of a colourless liquid in which red corpuscles, invisible to the naked eye owing to their small size, are floating about. It is these corpuscles which give blood its peculiar colour. Milk is also a transparent liquid, containing microscopic drops of fat, which rise to the top and form cream when the milk is left at rest. It is possible to extract from every non-homogeneous substance those homogeneous substances of which it is made up. Thus orthoclase may be separated from porphyry by breaking it off. So also gold is extracted from auriferous sand by washing away the mixture of clay and sand. Chemistry deals only with the homogeneous substances met with in nature, or extracted from natural or artificial non-homogeneous substances. The various mixtures found in

are made up, of the transformations of these substances ³ into each other, and of the phenomena ⁴ which accompany such transformations. Every chemical change, or reaction,⁵ as it is called, can only take place under a condition of most intimate and close contact of the reacting substances,⁶ and is determined by forces peculiar to the smallest invisible

nature form the subjects of other natural sciences—such as geology, botany, zoology, anatomy, &c. Substances can only be investigated by their *properties* or by their relations to our organs of sense and to other substances and bodies, but of itself matter is beyond the grasp of our understanding; for there is something in its nature which is self-existent and foreign to our understanding and spirit. If at the present day matter is represented as composed of individual mobile atoms, this is, in my opinion, only a scheme (a method or expedient for facilitating study) based originally on the structure of the visible (sidereal, solar) universe, which is actually composed of separate stars, like the sun, of planets and their satellites, of meteorites, and of the special ether which has the faculty of transmitting light and other forms of energy and motion, all of these being united in one harmonious whole. There is a great charm in the idea that the most minute parts of nature should be constructed on the same plan as the most gigantic, but it is far from proved that such is actually the case. It does not follow, however, because matter in itself is incomprehensible to us, that the study of matter is beyond our faculties if we follow the path of inductive reasoning (inaugurated by Bacon). This is evident from the fact that, by gradually investigating matter, man gains a greater and greater mastery over it, makes more and more accurate predictions concerning it, and finds wider and more frequent applications of it for satisfying his needs. In fact, there is no reason to anticipate any limit to our knowledge of, and dominion over, matter.

³ The name 'body' is given to a substance bounded by a surface or possessing shape. The earth, as a part of the solar system, is a body. A crystal, a plant, a house, are all bodies. It is evident that, in general, knowledge concerning matter is knowledge concerning bodies. Chemistry does not deal with bodies but with substances. However in ordinary usage the words 'body' and 'substance' are very often confused. Thus we speak of chemically simple and compound 'bodies' when we should, of course, use the word 'substances.'

⁴ All those events which are accomplished by substances in time are termed 'phenomena.' Phenomena in themselves form the fundamental subject of the study of physics. Motion is the primary and most easily understood form of phenomenon, and therefore we endeavour to reason about other phenomena as clearly as when dealing with motion. For this reason mechanics, which treats of motion, forms the fundamental science of natural philosophy, and in all other sciences endeavour is made to reduce the phenomena with which they are concerned to mechanical principles. Astronomy was the first to take to this path of reasoning, and succeeded in many cases in resolving astronomical into purely mechanical phenomena. And so, under the present state of knowledge, it is inevitably necessary to recognise the separate categories, motion and matter; and as chemistry is more closely concerned with the various forms of the latter, it should, together with mechanics, or the study of motion, lie at the basis of natural science.

⁵ The verb 'to react' means to act or change chemically.

⁶ If a phenomenon proceeds at visible or measurable distances (as, for instance, magnetic attraction or gravity), it cannot be described as chemical, since these phenomena only take place at distances immeasurably small and undistinguishable to the eye or the microscope; that is to say, they are purely molecular. Even Newton recognised, however, that it was impossible to comprehend the influence of bodies on each other (for instance attraction) without the agency of some medium situated between them. And this still holds good. Therefore a 'vacuum' is not admitted in modern science, but all so-called vacua, or spaces void of air, are considered to be filled with 'ether,' which was first regarded as the medium transmitting light waves, and afterwards as a means of

particles (molecules) of matter. We must distinguish three chief classes of chemical transformations.

1. *Combination* is a reaction in which the union of two substances yields a new one, or generally, from a given number of substances, a lesser number is obtained. Thus, by heating a mixture of iron and sulphur⁷ a single new substance is produced, iron sulphide, in which the constituent substances cannot be distinguished even under the highest magnification. Before the reaction the iron could be separated from the mixture by a magnet, and the sulphur by dissolving it in certain oily liquids;⁸ in general, before combination they might be mechanically separated from each other, but after combination the two substances penetrate into each other, and are then neither mechanically separable nor individually distinguishable. As a rule, reactions of direct combination are accompanied by an evolution of heat, and the common case of combustion, evolving heat, consists in the combination of the combustible substance with a portion (the oxygen) of the atmosphere, the gases and vapours contained in the flame and smoke representing the products of the combination.

explaining the action of attractions at a distance as well as magnetic and electrical phenomena. Without entering into these conceptions, which are more or less hypothetical (like that of the chemical elements), it may not be superfluous to mention that chemical theories lie beyond the hypothesis of ether, and that, judging from our present knowledge, chemical reactions do not proceed through the medium of ether, as they only take place by actual contact. It appears to me, therefore, that the chemism of substances possesses a certain simplicity and elementary character, and I foresee that chemistry may some day lead to an explanation of our conception regarding matter. In this sense chemical phenomena are more real to the understanding than physical or mechanical phenomena. Taking into consideration the comparative youth of this branch of natural science and the speciality of the phenomena it treats of, it seems to me that the province of chemical generalisations will rapidly extend, just as the applications of chemistry to the industries are extending at the present day. This forms the peculiar charm of chemistry, and especially of physico-chemical research. If the astronomer grasps the infinitely great in its highest reality, the chemist embraces the infinitely small, and science strives to attain the infinite and everlasting, unfettered by the finite and temporal.

⁷ For this purpose a piece of iron may be made red-hot in a forge, and then placed in contact with a lump of sulphur, when iron sulphide will be obtained as a molten liquid, the combination being accompanied by an appreciable increase in the glow of the iron. Or else iron filings are mixed with powdered sulphur in the proportion of 5 parts of iron to 3 of sulphur, and the mixture placed in a glass tube, which is then heated at one part. Combination does not commence without the aid of external heat, but when once started in any portion of the mixture it extends throughout the entire mass, because the portion first heated, in forming iron sulphide, evolves sufficient heat to raise the adjacent parts of the mixture to the temperature required for starting the reaction. The rise in temperature thus produced is so high as to soften the glass tube.

⁸ Sulphur dissolves slightly in many thin oils, and to a greater extent in carbon bisulphide and some other liquids. Iron is insoluble in carbon bisulphide, and the sulphur can therefore be dissolved away from the iron, so long as the two are not chemically combined.

2. Reactions of *decomposition* are the reverse of those of combination, that is, one substance gives two, or, in general, a given number of substances yields a greater number. Thus, by heating wood (and also coal and many animal or vegetable substances) without access to air, a combustible gas, a watery liquid, resin or tar, and carbon are obtained. It is in this way that tar, illuminating gas, and charcoal are prepared on a large scale.⁹ All limestones, for example, flagstones, chalk, or marble, when heated to redness are decomposed into lime and a peculiar gas called carbonic anhydride. A similar decomposition, taking place, however, at a much lower temperature, proceeds with the green copper carbonate which is contained in natural malachite. This example will be studied more in detail presently. Whilst heat is evolved in the ordinary reactions of combination, it is, on the contrary, generally absorbed in reactions of decomposition.

3. The third class of chemical reactions—where the number of reacting substances is equal to the number of substances formed—may be considered as a simultaneous decomposition and combination. If, for instance, two compounds A and B are taken and they react on each other, forming the substances C and D; then supposing that A is decomposed into D and E, and that E combines with B to form C, we have a reaction in which two substances A (or D E) and B were taken and two others C (or E B) and D were produced. Such reactions ought to be classed under the general term of reactions of '*rearrangement*,' and the particular case where two substances give two fresh ones, reactions of '*substitution*' or '*double decomposition*.'¹⁰ Thus, if a piece of iron be immersed in a solution of blue vitriol (copper sulphate), copper is formed—or, rather, separated out, and green vitriol (iron sulphate), which only differs from the blue vitriol in that the iron has replaced the copper, is obtained in solution. In this manner iron may be coated with copper, or copper with silver; such reactions are frequently made use of in practice.

⁹ Decomposition of this kind is termed '*dry distillation*,' because, just as in distillation, the substance is heated and vapours are given off which, on cooling, condense into liquids. In general, decomposition, in absorbing heat, presents much in common with a physical change of state—such, for example, as that of a liquid into a gas. Deville likened complete decomposition to boiling, and compared partial decomposition, in which a portion of a substance is not decomposed in the presence of its products of decomposition (or dissociation), with evaporation.

¹⁰ A reaction of rearrangement may in certain cases take place with one substance only; that is to say, a substance may by itself change into a new *isomeric* form. Thus, for example, if hard yellow sulphur be heated to a temperature of 250° and then poured into cold water, it gives, on cooling, a soft brown variety. Cases of isomerism indicate the possibility of an internal rearrangement in a substance, and are the result of an alteration in the grouping of the same elements, just as a certain number of balls may be grouped in figures and forms of different shapes.

The majority of the chemical changes which occur in nature and are made use of technically are very complicated, as they consist of an association of many separate and simultaneous combinations, decompositions, and replacements. It is chiefly due to this natural complexity of chemical phenomena that for so many centuries chemistry did not exist as an exact science; that is to say, that although many chemical changes were known and made use of,¹¹ yet their real nature was unknown, and they could not be predicted or directed at will. Another reason for the tardy progress of chemical knowledge is the participation of gaseous substances, especially air, in many reactions. The true comprehension of air as a ponderable substance, and of gases in general as peculiar elastic and dispersive forms of matter, was only arrived at in the sixteenth and seventeenth centuries, and it was only after this that the transformations of substances could form a science. Up to that time, without understanding the invisible, but ponderable, gaseous and vaporous forms of matter, it was impossible to obtain any fundamental chemical knowledge, because the gases formed or used up in any reaction escaped notice. It is easy, from the impression conveyed to us by the phenomena we observe, to form the opinion that matter is created and destroyed; a whole mass of trees burn, and there only remains a little charcoal and ash, whilst from one small seed there grows little by little a majestic tree. In one case matter seems to be destroyed, and in the other to be created. This conclusion is arrived at because the formation or consumption of gases, being under the circumstances invisible to the eye, is not observed. When wood burns, it undergoes a chemical change into gaseous products, which escape as smoke. The substance of the wood is not lost; it is only converted into gaseous form by a chemical process. A very simple experiment will prove this. By collecting the smoke it may be observed that it contains gases which differ entirely from air, being incapable of supporting either combustion or respiration. These gases may be weighed, and it will then be seen that their weight exceeds that of the wood taken. This increase in weight arises from the fact that, in burning, the component parts of the wood combine with a portion of the air; in like manner iron increases in weight by rusting. When gunpowder is burnt its substance is not destroyed, but only converted into gases and smoke. So also in the growth of a tree: the seed does not increase in mass of itself and from itself, but grows because it absorbs gases from

¹¹ For example, the conversion of the juice of grapes, containing a saccharine principle (glucose), into wine or vinegar, and the extraction of metals from the ores found in the earth's crust.

the atmosphere and sucks water and substances dissolved therein from the earth through its roots. The sap and solid substances which give plants their form are produced from these absorbed gases and liquids by complicated chemical processes directed by forces acting in the living organism. Plants not only do not increase in size, but die, in a gas which does not contain the nutrient constituents of air. When moist substances dry they decrease in weight; when water evaporates we know that it does not disappear, but will return from the atmosphere as rain, dew, and snow. When water is absorbed by the earth, it does not disappear there for ever, but accumulates somewhere underground, whence it afterwards flows forth as a spring. Thus matter does not disappear and is not created, but only undergoes various physical and chemical transformations—that is to say, changes its locality and form. Matter remains in the same quantity as before; in a word it is, so far as we are concerned, everlasting. It was difficult to submit this simple and primary chemical principle to investigation, but when once made clear it rapidly spread, and now seems as natural and simple as many truths which have been acknowledged for ages. The philosophers of ancient Greece, and also Mariotte and other savants of the seventeenth century, suspected the indestructibility or conservation of matter, but they made no efforts to express it, or to make use of it for scientific purposes. The experiments by means of which this simple law was arrived at were made during the latter half of the eighteenth century by the founder of modern chemistry, LAVOISIER, the French Academician and tax farmer.^{11a} The numerous experiments of this savant were conducted with the aid of the balance, which is the only means of directly and accurately determining the quantity of matter.

By weighing all the substances, and also the apparatus, used in every experiment, and then weighing the substances obtained after the chemical change, Lavoisier found that the sum of the weights of the substances formed was always equal to the sum of the weights of the substances taken; or, in other words: **Matter is not created and does not disappear**—i.e., *matter is everlasting*—so that the mass (weight) of matter in nature remains unchanged or constant. This

^{11a} The portrait of Lavoisier is placed at the beginning of this work because he established the fundamental law of our science on an indestructible basis, and should be regarded as the founder of modern scientific chemistry. Lavoisier was born on August 26, 1743, soon after the death of Newton, and his name must rank with those of Galileo and Newton. The closing days of his life were passed during the Reign of Terror, and he was beheaded at Paris, together with 27 other tax-farmers, on May 8, 1794; but his works and ideas have rendered him immortal. A monument, the cost of which was defrayed by international subscription, was erected in his honour in Paris in the year 1900.

expression naturally includes a hypothesis, but it serves to express concisely the following lengthy period: That in all experiments, and in all the investigated phenomena of nature, it has never been observed that the weight of the substances formed was less or greater (as far as accuracy of weighing permits ¹²) than the weight of the substances originally taken, and as weight is proportional to mass ^{12a} or quantity of matter, it follows that no one has ever succeeded in observing a disappearance of matter or its appearance in fresh quantities. The law of the indestructibility of matter endows all chemical investigations with exactitude, as on its basis an equation may be formed for every chemical reaction. If in any reaction the weights of the substances taken be designated by the letters A, B, C, &c., and the weights of the substances formed by the letters M, N, O, &c., then



Therefore, should the weight of one of the reacting or resultant substances be unknown, it may be determined by solving this equation.

By applying the law of the indestructibility of matter, and by making use of the chemical balance, the chemist can never lose sight of any one of the reacting or resultant substances. Should such an oversight be made, it will at once be remarked that the sum of the weights of the substances taken is unequal to the sum of the weights of the substances formed. It is absolutely necessary, in beginning the study of chemistry, to become familiar with the simple truth which is expressed by this law, and for this purpose several examples illustrating its application will now be cited.

¹² The experiments conducted by the Belgian savant Stas (described in detail in Chap. XXIV. on Silver) form some of the most accurate of the researches which go to prove that the weight of matter is not altered in chemical reactions, as he weighed extremely accurately (introducing all the necessary corrections) the reacting and resultant substances. Landolt (1893) carried on various reactions in inverted and sealed glass U-tubes, and on weighing the tubes before reaction (when the reacting solutions were separated in each of the branches of the tubes) and afterwards (when the solutions had been well mixed by shaking) found either that the weight remained perfectly constant or that the variation was so small (for instance, 0.2 milligram) that it must be ascribed to the inevitable errors of weighing. It is now possible to weigh weights (like the Russian standard platino-iridium pound) with an accuracy of one ten-millionth part of their weight, as is done in the St. Petersburg Weights and Measures Department. Such a degree of accuracy (greater than in any other relative but direct measurement) can only be attained by observing a great many precautions, and only when dealing with such hard and invariable bodies as platino-iridium weights. In ordinary chemical works, especially when weighing glass vessels, liquids or gases, an accuracy of one millionth (that is, a milligram in a kilogram) is scarcely attainable owing to the effect of various corrections in weighing (reducing to vacuum), friction of surfaces, &c., on the ultimate result.

^{12a} The idea of the mass of matter was first given an exact form by Galileo (died 1642), and more especially by Newton (born 1643, died 1727), in the glorious epoch marking the development of the principles of inductive reasoning enunciated by Bacon and Descartes in their philosophical treatises.

1. It is well known that iron rusts in damp air,¹³ and that when heated to redness in air it becomes coated with scale (oxide) which has, like rust, the appearance of an earthy substance and resembles some of the iron ores from which metallic iron is extracted. If the iron is weighed before and after the formation of the scale or rust, it will be found that the metal has increased in weight during the operation.¹⁴ It can easily be proved that this increase in weight is accomplished at the expense of the atmosphere, and mainly, as Lavoisier proved, at the expense of that portion which is called oxygen, and which supports combustion. In fact, in a vacuum, or in gases which do not contain oxygen, for instance, in hydrogen or nitrogen, iron neither rusts nor becomes coated with scale. Had the iron not been weighed, the participation of the oxygen of the atmosphere in its transformation into an earthy substance might easily have passed unnoticed, as was the case prior to the time of Lavoisier, when phenomena like the above were, for this reason, misunderstood. It is evident from the law of the indestructibility of matter that as iron increases in weight in its conversion into scale, the latter must be a more complex substance than iron itself, and its formation is due to a reaction of combination. We might form an entirely wrong opinion about this transformation, and might consider, for instance, the scale to be a simpler substance than iron, and explain the formation of scale as due to the removal of something from the iron. Such, indeed, was the general opinion prior to Lavoisier, when it was held that iron contained a certain unknown substance called 'phlogiston,' and that scale was iron deprived of this supposed substance.

2. When copper carbonate (in the form of a powder, or as the well-known green mineral called 'malachite,' which is used both for making ornaments and as an ore for the extraction of copper) is heated to

¹³ By covering iron with enamel, varnish, an unrustable metal (such as nickel), a coating of paraffin, or some similiar substance, it may be protected from the air and moisture, and so kept from rusting.

¹⁴ Such an experiment may easily be made by taking the finest (unrusted) iron filings (ordinary filings must be first washed in ether to remove traces of grease, then dried, and passed through a very fine sieve). The filings thus obtained are capable of burning directly in air (by oxidising or forming scale), especially when they hang (attracted) from a magnet. A compact piece of iron does not burn in air, but spongy iron glows and smoulders like tinder. In making the experiment, a horseshoe magnet is fixed, with the poles downwards, on one arm of a fairly sensitive balance, and the iron filings are applied to the magnet (on a sheet of paper) so as to form a beard or fringe about the poles. The balance pan should be exactly under the filings on the magnet, in order that any filings which might fall should not alter the weight. The filings, having been weighed, are ignited by applying the flame of a candle or lamp: they easily take fire, and go on burning by themselves, forming scale. When the combustion is ended, it will be clear that the iron has increased in weight; from $5\frac{1}{2}$ parts by weight of iron filings taken, there are obtained, by complete combustion, about $7\frac{1}{2}$ parts by weight of scale.

redness it changes into a black substance called 'copper oxide.'¹⁵ This black substance is also obtained by heating copper to redness in air—that is, it is the scale or oxidation product of copper. The weight of the black oxide of copper left is less than that of the copper carbonate originally taken, and therefore we consider the reaction which occurred to have been one of decomposition, and that by it something was separated from the green copper carbonate; in fact, by closing the orifice of the vessel in which the copper carbonate is heated, with a well-fitting cork, through which passes a gas delivery tube¹⁶ the end of which is immersed under water, it will be observed that during the heating a gas is formed which bubbles through the water. This gas can be easily collected, as will presently be described, and it will be found to differ essentially from air in many respects; for instance, a burning taper is extinguished in it just as if it had been plunged into water. If weighing had not proved to us that some substance had been separated, the formation of the gas might easily have escaped our notice, as it is colourless and transparent like air. The carbonic anhydride evolved may be weighed,¹⁷ and it will be seen that the sum of the

¹⁵ For the purpose of experiment it is most convenient to take copper carbonate, which may be prepared by the experimenter himself, by adding a solution of sodium carbonate to a solution of copper sulphate. The precipitate (deposit) so formed is collected on a filter, washed, and dried. The decomposition of copper carbonate into copper oxide and carbonate anhydride is effected by so moderate a heat that it may be carried out in a glass vessel heated by a lamp. For this purpose a thin glass tube closed at one end, and called a 'test tube,' may be employed, or else a vessel called a 'retort.' The experiment is carried on, as described in example 3 on p. 11, by collecting the carbonic anhydride over water, as will be afterwards explained.

¹⁶ Gas delivery tubes are usually made of glass tubing of various diameters and thicknesses. If of small diameter and thickness, a glass tube is easily bent by heating in a gas jet or the flame of a spirit lamp, and it may also be easily divided at a given point by making a scratch with a file and then breaking the tube at this point with a sharp jerk. These properties, together with their impermeability, transparency, hardness, and regularity of bore, render glass tubes most useful in experiments with gases. A glass gas delivery tube may be hermetically fixed into a vessel by fitting it into a perforated cork, which should be soft and free from flaws, and fixing the cork into the orifice of the vessel. To protect the cork from the action of gases it is sometimes previously soaked in melted paraffin wax, or else replaced by an indiarubber stopper.

¹⁷ Gases, like all other substances, may be weighed, but, owing to their extreme lightness and the difficulty of dealing with them in large masses, they can only be weighed on very sensitive balances; that is, on such as, with a considerable load, indicate a very small change in the weight—for example, a milligram on a load of 1,000 grams. In order to weigh a gas, a glass globe furnished with a tight-fitting stop-cock is first of all exhausted of air by an air-pump (a Sprengel pump is the best), after which the stop-cock is closed, and the exhausted globe weighed. If the gas to be weighed is then let into the globe, its weight can be determined from the increase in the weight of the globe. It is necessary, however, that the temperature and pressure of the air about the balance should remain the same for both weighings, as the weight of the globe in air varies (according to the laws of hydrostatics) with the density of the latter. The volume of the air displaced, and its weight, must therefore be determined by observing

weights of the black copper oxide and the carbonic anhydride is equal to the weight of the copper carbonate ¹⁸ originally taken.

3. When red oxide of mercury (which is formed as mercury rust by heating mercury in air) is heated, it is decomposed, like copper carbonate (only by heating more slowly and at a somewhat higher temperature), with the formation of the peculiar gas, oxygen. For this purpose the oxide of mercury is placed in a glass tube or retort, ¹⁹ to

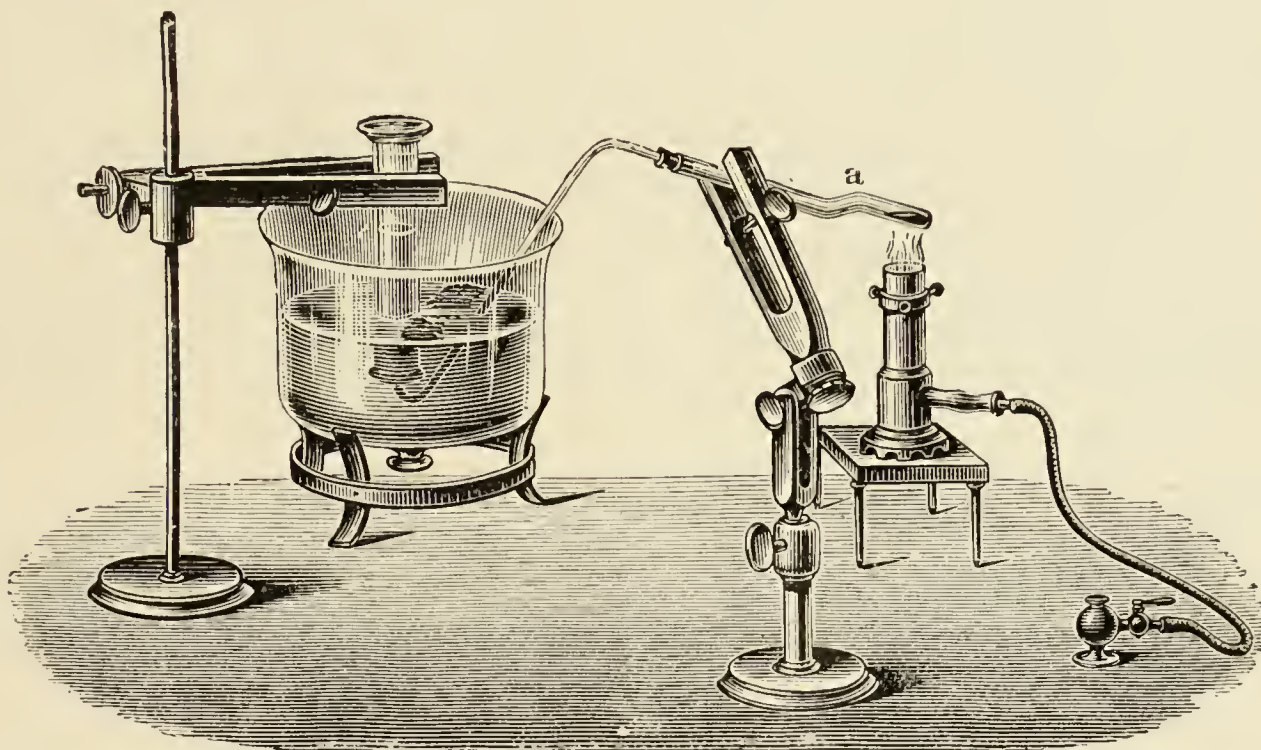


FIG. 1.—Apparatus for the decomposition of red mercury oxide.

which a gas delivery tube is attached by means of a cork. This tube is bent downwards, as shown in the drawing (fig. 1), and its open end

the temperature, density, and moisture of the atmosphere during the time of the experiment. This will be partly explained later, but may be studied more in detail by physics. Owing to the complexity of all these operations, the mass of a gas is usually determined from its volume and its density, i.e. the weight of unit volume.

¹⁸ The copper carbonate should be dried before weighing, as otherwise—besides copper oxide and carbonic anhydride—water will be obtained in the decomposition. Water enters into the composition of malachite, and has therefore to be allowed for. The water produced in the decomposition may be all collected by absorbing it in sulphuric acid or calcium chloride, as will be described further on. In order to dry a salt it must either be heated at about 100° until its weight remains constant, or be placed under an air-pump over sulphuric acid, as will also be presently described. As water is met with almost everywhere, and as it is absorbed from the air by many substances, the possibility of its presence should never be lost sight of in weighing.

¹⁹ As the decomposition of red oxide of mercury requires so high a temperature—approaching a red heat—as to soften ordinary glass, it is necessary for this experiment to take a retort (or test tube) made of hard glass, which is able to stand high temperatures without softening. For the same reason the lamp used must give a strong heat and a large flame, capable of embracing the whole of the bottom of the retort, which should be as small as possible for the convenience of the experiment.

immersed in a vessel filled with water, called a pneumatic trough.²⁰ When the gas begins to be evolved in the retort it is obliged, having no other outlet, to escape through the gas delivery tube into the water in the pneumatic trough, and its evolution will therefore be rendered visible by the bubbles coming from this tube. On heating the retort containing the mercury oxide, the air contained in the apparatus is first partly expelled, owing to its expansion by heat, and after this the peculiar gas called 'oxygen' is evolved and may be easily collected as it comes off. For this purpose a vessel (an ordinary cylinder, as in the drawing) is filled quite full with water and its mouth closed; it is next inverted and the mouth dipped under the water in the trough and then opened. The cylinder will remain full of water—that is, the water will remain

²⁰ The pneumatic trough may naturally be made of any material (china, earthenware, metal, &c.), but a glass one, as shown in the drawing, is generally used, as it allows the progress of the experiment to be better observed. For this reason, and on account of the ease with which they are kept clean, and also owing to the fact that glass is not

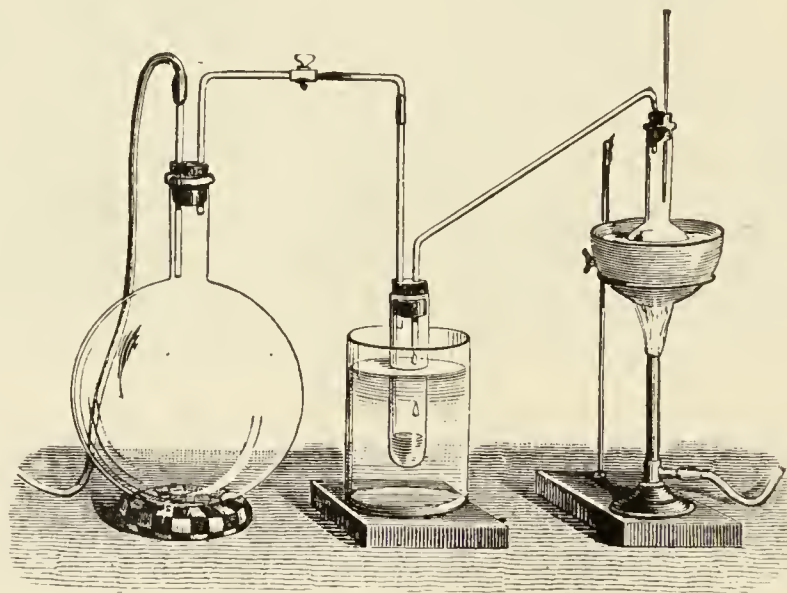


FIG. 2.—Apparatus for distilling, under a diminished pressure, liquids which decompose at their boiling-points under the ordinary pressure. The apparatus in which the liquid is distilled is connected with a large globe from which the air is pumped out; the liquid is heated, and the receiver cooled.

acted on by many substances which affect other materials (for instance, metals), glass vessels of all kinds are preferred to any others for chemical experiments. A glass vessel may be heated without any danger if the following precautions be observed: 1st, it should be made of thin glass, as otherwise it is liable to crack from the bad heat-conducting power of glass; 2nd, it should be surrounded by a liquid or by sand (fig. 2), or sand bath as it is called; or else it should stand in a current of hot gases without touching the fuel from which they proceed, or in the flame of a smokeless lamp. A common candle or lamp forms a deposit of soot on a cold object placed in the flame. The soot interferes with the transmission of heat, so that a glass vessel when covered with soot often cracks. And for this reason spirit lamps, which burn with a smokeless flame, or gas burners of a peculiar construction, are used. In the Bunsen burner the gas is previously mixed with air, after which it burns with a non-luminous and smokeless flame. On the other hand, if an ordinary lamp (petroleum or benzine) does not smoke it may be used without danger for heating a glass vessel, provided the glass is placed well above the flame in the current of hot gases. In all cases the heating should be begun very carefully and the temperature gradually raised.

at a higher level in it than in the surrounding vessel, owing to the atmospheric pressure. The mouth of the cylinder is placed over the end of the gas delivery tube,²¹ and the bubbles issuing from the latter will rise into the cylinder and displace the water contained in it. Gases are generally collected in this manner. When a sufficient quantity of gas has accumulated in the cylinder it can be clearly shown that it is not air, but another gas which is distinguished by its capacity for vigorously supporting combustion. In order to show this, the cylinder is closed under water, and removed from the bath; its mouth is then turned upwards, and a smouldering taper plunged into it. As is well known, a smouldering taper will be extinguished in air, but in the gas which is given off from red mercury oxide it burns clearly and vigorously, showing the property possessed by this gas for supporting combustion more energetically than air, and thus enabling it to be distinguished from the latter. It may be observed in this experiment that, besides oxygen, there is also formed metallic mercury, which, volatilising at the high temperature required for the reaction, condenses on the cooler parts of the retort in the form of a mirror or in globules. Thus two substances, mercury and oxygen, are obtained by heating red mercury oxide. In this reaction, from a single substance, two new ones are produced—that is, a decomposition has taken place. The means of collecting and investigating gases were known before Lavoisier's time, but he first showed the real part they played in the processes of many chemical changes which before his era were either wrongly understood (as will be afterwards explained) or not explained at all, but only observed in their superficial aspects. This experiment on red oxide of mercury has a special significance in the history of chemistry contemporary with Lavoisier, because the oxygen gas which is here evolved is contained in the atmosphere, and plays a most important part in nature, especially in the respiration of animals, in combustion in air, and in the formation of rusts or scorïæ (earths, as they were then called) from metals—that is, of earthy substances, like the ores from which metals are extracted.

4. In order to illustrate by experiment one more example of chemical change and the application of the law of the indestructibility of matter, we will consider the reaction between common table salt and lunar caustic, which is well known from its use in cauterising

²¹ In order to avoid the necessity of holding the cylinder, its open end is widened (and also ground so that it may be tightly closed with a ground-glass plate when necessary), and placed on a stand below the level of the water in the bath. This stand is called 'the bridge.' It has several circular openings cut through it, and the gas delivery tube is placed under one of these, and the cylinder for collecting the gas over it.

wounds. Both these substances are soluble in water. By taking clear solutions of each of these and mixing them together, it will at once be observed that a solid white substance is formed which settles to the bottom of the vessel, and is insoluble in water. This substance may be separated from the solution by filtering. This is at once evident from the fact that it does not dissolve in water. On evaporating the liquid which passes through the filter, it will be found to contain a new substance differing from both table salt and lunar caustic, but, like them, soluble in water. Thus table salt and lunar caustic, two substances soluble in water, produce, by their mutual chemical action, two new substances, one of which is insoluble in water whilst the other remains in solution. The water serves only to convert the reacting substances into a liquid and mobile state. If the lunar caustic and salt be dried ²² and weighed, and if about $58\frac{1}{2}$ grams ²³ of the latter and 170 grams of the former be taken, then $143\frac{1}{2}$ grams of insoluble silver chloride and 85 grams of soluble sodium nitrate will be obtained. The sums of the weights of the reacting and of the resultant substances are seen to be similar ($228\frac{1}{2}$ grams), which follows necessarily from the law of the indestructibility of matter.

Accepting the truth of the above law, the question naturally arises as to whether there is any limit to the various chemical transformations, or are they unrestricted in number—that is to say, is it possible from a given substance to obtain an equal quantity of any other substance? In other words, does there exist a perpetual and infinite change of one kind of material into every other kind, or is the cycle of these transformations limited? This is the second essential problem of chemistry, a question concerning the quality of matter, and one, it is evident, more complicated than the question of quantity. It cannot be solved by a mere superficial glance at the subject. Indeed, on seeing how all the varied forms and colours of plants are built up from air and the elements of the soil, and how metallic iron can be transformed into colours such as inks and Prussian blue, we might be led to think that

²² Drying is necessary in order to remove any water which may be held in the salts (see note 18).

* ²³ The exact weights of the reacting and resulting substances are determined with the greatest difficulty, not only from possible inexactitude of the balance (every weighing is only correct within the limits of sensitiveness of the balance) and weights used, not only from the difficulty in making corrections for the weight of air displaced by the vessels containing the substances weighed and by the weights themselves, but also from the hygroscopic nature of many substances (and vessels) causing absorption of moisture from the atmosphere, and from the difficulty of not losing any of the substance to be weighed in the several operations (filtering, evaporating, drying, &c) which have to be performed before arriving at a final result. All these circumstances have to be taken into consideration in exact researches.

there is no end to the qualitative changes to which matter is susceptible. But, on the other hand, everyday experience compels us to acknowledge that food cannot be made out of a stone, nor gold out of copper. Thus a definite answer can only be looked for in a close and diligent study of the subject, and the problem has been solved in different ways at different times. In ancient times the opinion most generally held was that everything visible was composed of four elements—Air, Water, Earth, and Fire. The origin of this doctrine can be traced far back into the confines of Asia, whence it was handed down to the Greeks, and very fully expounded by Empedocles, who lived before 460 B.C. This doctrine was not the result of exact research, but apparently owes its origin to the clear division of bodies into gases (like air), liquids (like water), and solids (like the earth), and to the recognition of the changes brought about in these by fire, i.e. heat. The Arabs attempted to solve the question by experimental methods, and, by way of Spain, they introduced a taste for the study of similar problems into Europe, where from that time there appear many adepts in chemistry, which was regarded as an unholy art, and called ‘alchemy.’ As the alchemists were ignorant of any exact law which could serve as a starting-point for their researches, they obtained most anomalous results. Their chief service to chemistry was that they made a number of experiments, and discovered many new chemical transformations; but it is well known how they solved the fundamental problem of chemistry. Their view may be taken as a positive acknowledgment of the infinite transmutability of matter, for they aimed at discovering the Philosopher’s Stone, capable of converting everything into gold and diamonds, and of making the old young again. This solution of the question was afterwards completely overthrown, but it must not be thought that the hopes held by the alchemists were only the fruit of their imaginations. The first chemical experiments might well lead them to such conclusions. They took, for instance, the bright metallic mineral galena, and extracted metallic lead from it. Thus they saw that from a metallic substance which is unfitted for use they could obtain another metallic substance which is ductile and valuable for many technical purposes. Furthermore, they took this lead and obtained silver, a still more valuable metal, from it. Thus they might easily conclude that it is possible to ennoble metals by means of a series of transmutations—that is to say, to obtain from them those which are more and more precious. Having got silver from lead, they assumed that it would be possible to obtain gold from silver. The imperfection of their work is to be ascribed to the fact that, as a rule, they paid little attention to quantities, and qualitative data are very often subjective

and conditional. Had they done so, they would have learnt that the weight of the lead was much less than that of the galena from which it was obtained, and the weight of the silver infinitesimal compared with that of the lead. Had they looked more closely into the process of the extraction of silver from lead (and silver at the present time is chiefly obtained from lead ores), they would have seen that the lead does not change into silver, but that it only contains a certain small quantity of the latter, and this amount having once been separated from the lead it cannot by any further operation give more. The silver which the alchemists extracted from the lead was in the lead, and was not obtained by a chemical change of the lead itself. This is now well known from experiment, but the first view of the nature of the process was very likely to be an erroneous one.²⁴ The methods of research adopted by the alchemists could give but little success, for they did not set themselves clear and simple questions, the answers to which would aid them to make further progress. But although they did not arrive at any exact law, they nevertheless left many new experimental data as an inheritance to chemistry; they investigated, in particular, the transformations proper to metals, and for this reason chemistry was for long afterwards entirely confined to the study of metallic substances.

In their researches the alchemists made frequent use of two chemical processes which are now termed 'reduction' and 'oxidation.' The rusting of metals, and in general their conversion from a metallic into an earthy form, is called 'oxidation,' whilst the extraction of a metal from an earthy substance is called 'reduction.' Many metals—for instance, iron, lead, and tin—are oxidised by simply heating in air, and may be again reduced by heating with carbon. Such oxidised metals are found in the earth and represent one type of metallic ores. Metals such as tin, iron, and copper, may be extracted from these ores by heating them together with carbon. All these processes were studied by the alchemists. Thus the alchemists knew of two forms of chemical change: the oxidation of metals and the reduction of the oxides so formed into metals. The explanation of the nature of these

²⁴ Indeed, in the majority of cases, the first explanation of a phenomenon which does not repeat itself in everyday experience under various aspects, but always in one form, or only at intervals and infrequently, is wrong. Thus the daily rising and setting of the sun and stars evoke the erroneous idea that the heavens move and that the earth stands still. This apparent truth is far from being the real one, and, as a matter of fact, is contradictory to it. Similarly, everyday experience concludes that iron is incombustible, whereas it burns not only as filings (see note 14) but even as wire, as we shall see later. In ordinary life we often reason at first sight with perfect accuracy, only because we are taught a right judgment by our daily experience. Naturally, experiment itself cannot give truth, but it makes it possible to destroy erroneous representations and to confirm in all their consequences those which are true.

two classes of chemical phenomena was the means for the discovery of the most important chemical laws. The first hypothesis on their nature is due to Becker, and more particularly to Stahl, a surgeon to the King of Prussia. In his 'Fundamenta Chemiæ,' 1723, Stahl states that all substances consist of an imponderable fiery substance called 'phlogiston' (*materia aut principium ignis non ipse ignis*), and of another element having particular properties for each substance. The greater the capacity of a body to undergo oxidation or combustion, the richer it is in phlogiston. Carbon contains it in great abundance. In oxidation or combustion phlogiston is emitted, and in reduction it is consumed or enters into combination. Carbon reduces earthy substances because it is rich in phlogiston, a portion of which it gives up to the substance reduced. Thus Stahl supposed a metal to be a compound substance consisting of phlogiston and an earthy substance or oxide. This hypothesis is distinguished for its very great simplicity, and for this and other reasons it acquired many supporters.²⁵

Lavoisier proved by means of the balance that every case of rusting

²⁵ It is true that Stahl was acquainted with a fact which directly disproved his hypothesis. It was already known (from the experiments of Geber, and more especially those of Ray in 1630) that metals increase in weight on oxidation, whilst, according to Stahl's hypothesis, they should decrease in weight because phlogiston is given up. Stahl speaks on this point as follows:—'I am well aware that on oxidation (transformation into earths) metals increase in weight. Not only does this fact not disprove my theory, but, on the contrary, it confirms it, for phlogiston is lighter than air, and, in combining with substances, strives to lift them, and so decreases their weight; consequently a substance which has lost phlogiston must be heavier.' This argument, it will be seen, is founded on a confused idea of phlogiston itself, since it was first defined as imponderable. The conception of imponderable phlogiston tallies well with the habit and methods of the past century, when recourse was had to imponderable fluids for explaining a large number of phenomena. Heat, light, magnetism, and electricity were explained as being peculiar imponderable fluids. In this sense the doctrine of Stahl corresponds entirely with the spirit of his time. If heat be now regarded as motion or energy, then phlogiston also should be considered in this light. In fact, in combustion, of coals, for instance, heat and energy are evolved and not combined with the coal, although the oxygen and coal do combine. Consequently the doctrine of Stahl contains the essence of a true representation of the evolution of energy, but naturally this evolution is only a consequence of the combination occurring between the coal and oxygen. As regards the history of chemistry prior to Lavoisier, besides Stahl's work, Priestley's *Experiments and Observations on different Kinds of Air* (London, 1790), and also Scheele's *Opuscula Chimica et Physica* (Lips., 1788-89, 2 vols.), must be recommended as the two leading works of the English and Scandinavian chemists showing the condition of chemical learning before the propagation of Lavoisier's views, and containing also many important observations which lie at the basis of the chemistry of our times. A most interesting memoir on the history of phlogiston is that of Radwell, in the *Philosophical Magazine*, 1868, in which it is shown that the idea of phlogiston dates very far back, that Basil Valentine (1394-1415), in the *Cursus Triumphalis Antimonii*, Paracelsus (1493-1541), in his work *De Rerum Natura*, Glauber (1604-1668), and especially John Joachim Becher (1625-1682), in his *Physica Subterranea*, all referred to phlogiston, but under different names.

of metals or oxidation, or of combustion, is accompanied by an increase in weight at the expense of the atmosphere. He formed, therefore, the natural opinion that the heavier substance is more complex than the lighter one.²⁶ Lavoisier's celebrated experiment, made in 1774, gave indubitable support to his views, which in many respects were contradictory to Stahl's doctrine. Lavoisier poured four ounces of pure mercury into a glass retort (fig. 3), the neck of which was bent as shown in the drawing and dipped into the vessel R S, also full of mercury, the projecting end of the neck being covered with a glass bell-jar P. The weight of all the mercury taken, and the volume of air remaining in the apparatus, that is, in the upper portion of the retort and under the bell-jar, were determined before beginning the experiment. It was most important in this experiment to know the volume of air, in order to learn what part it played in the oxidation of

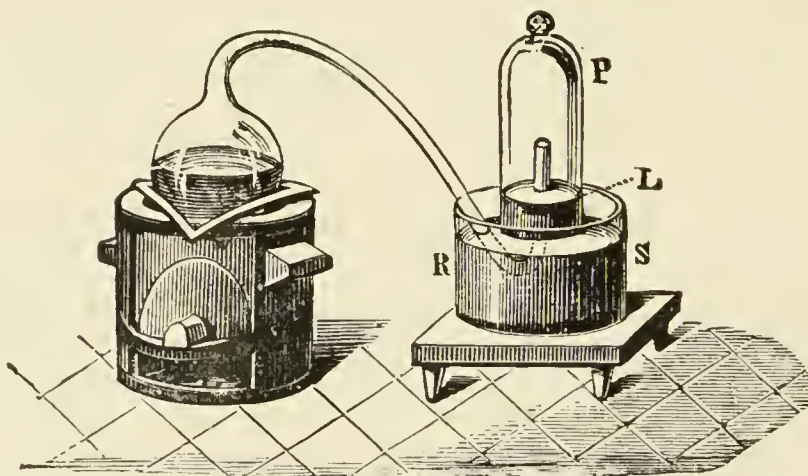


FIG. 3.—Lavoisier's apparatus for determining the composition of air and the reason of the increase in weight of metals when they are calcined in air.

the mercury, because, according to Stahl, phlogiston is emitted into the air, whilst, according to Lavoisier, the mercury in oxidising absorbs a portion of the air; consequently it was absolutely necessary to determine whether the amount of air increased or decreased during the oxidation of the metal. It was therefore most important to measure the volume of the air in the apparatus both before and after the

²⁶ An Englishman named Mayow, who lived a whole century before Lavoisier (in 1666), understood certain phenomena of oxidation in their true aspect, but was not able to develop his views with clearness or to support them by conclusive experiments; he cannot therefore be considered, like Lavoisier, as the founder of contemporary chemical learning. Science is a universal heritage, and therefore it is only just to give the highest honour in science, not to those who first enunciate a certain truth, but to those who are first able to convince others of its authenticity and to establish it for the general welfare. But scientific discoveries are rarely made all at once; as a rule, the first teachers do not succeed in convincing others of the truth they have discovered; with time, however, a true herald comes forward, possessing every means for making the truth apparent to all; but it must not be forgotten that such are indebted to the labours of many others and to the mass of data accumulated by them. Such was Lavoisier, and such are all the great founders of science.

experiment. For this purpose it was necessary to know the total capacity of the retort, the volume of the mercury poured into it, the volume of the bell-jar above the level of the mercury, and also the temperature and pressure of the air at the time of its measurement. From these data the volume of air contained in the apparatus and isolated from the surrounding atmosphere could be determined. Having arranged his apparatus in this manner, Lavoisier heated the retort for a period of twelve days at a temperature near the boiling point of mercury. The mercury became covered with a quantity of small red scales; that is, it was oxidised or converted into an earth (like lime). This substance is the same mercury oxide which has already been mentioned (example 3). After the lapse of twelve days the apparatus was cooled, and it was then seen that the volume of the air in the apparatus had diminished during the time of the experiment; a result directly contradictory to the views of the German investigator. Out of 50 cubic inches of air originally taken, there only remained 42. Lavoisier's experiment led to other equally important results. The weight of the air taken decreased by as much as the weight of the mercury increased in oxidising; that is, part of the air was not destroyed, but only combined with mercury. This portion of the air may be again separated from the mercury oxide, and has, as we have seen (example 3), properties different from those of air. It is called 'oxygen.' That portion of the air which remained in the apparatus and did not combine with the mercury does not oxidise metals, and cannot support either combustion or respiration, so that a lighted taper is immediately extinguished if it be dipped into the gas which remains in the bell-jar. 'It is extinguished in the residual gas as if it had been plunged into water,' writes Lavoisier in his memoirs. This gas is called 'nitrogen.' Thus air is not a simple substance, but consists of two gases, oxygen and nitrogen, and therefore the opinion that air is an elementary substance is erroneous. The oxygen of the air is absorbed in combustion and in the oxidation of metals, and the earths produced by the oxidation of metals are substances composed of oxygen and a metal. By mixing the oxygen with the nitrogen the same air as was originally taken is re-formed. It has also been shown by direct experiment that on reducing an oxide with carbon the oxygen contained in the oxide is transferred to the carbon, and gives the same gas as is obtained by the combustion of carbon in air. This gas is therefore a compound of carbon and oxygen, just as the earthy oxides are composed of metals and oxygen.

The many examples of the formation and decomposition of substances which are met with convince us that the majority of substances

with which we have to deal are compounds made up of several other substances. By heating chalk (or else copper carbonate, as in the second example) we obtain lime and the same carbonic acid gas which is produced by the combustion of carbon. On bringing lime into contact with this gas and water, at the ordinary temperature, we again obtain the compound, carbonate of lime, or chalk. Therefore chalk is a compound. So also are those substances from which it may be built up. Carbonic anhydride is formed by the combination of carbon and oxygen, and lime is produced by the oxidation of a certain metal called 'calcium.' By resolving substances in this manner into their component parts we arrive at last at such as are indivisible into two or more substances by any means whatever, and which cannot be formed from other substances. All we can do is to make such substances either combine with one another or act on other substances. Substances which cannot be formed from or decomposed into others are termed **simple substances** (elements). Thus all homogeneous substances may be classified into simple and compound substances. This view was introduced and established as a scientific fact during the lifetime of Lavoisier. The number of these elements is very small in comparison with the number of compound substances which are formed by them. At the present time only seventy-five elements are known with certainty to exist. Some of them are very rarely met with in nature, or are found only in very small quantities. The number of elements with whose compounds we commonly deal in everyday life does not exceed twenty-five at the present time.

Elements cannot be transmuted into one another—at least up to the present not a single case of such a transformation has been met with; it may therefore be said that as yet it is impossible to transmute one metal into another. And, notwithstanding the number of attempts which have been made in this direction, no fact has been discovered which could in any way support the idea of the complexity of such well-known elements²⁷ as oxygen, iron, sulphur, &c. Therefore, from its very conception, an element is not susceptible to reactions of decomposition.²⁸

²⁷ Many of the ancient philosophers assumed the existence of one elementary form of matter. This idea still appears in our times, in the constant efforts which are made to reduce the number of the elements; to prove, for instance, that bromine contains chlorine, or chlorine, oxygen. By many methods, founded both on experiment and theory, has it been tried to prove the compound nature of the elements. All labour in this direction has as yet been in vain, and the assurance that elementary matter is not so homogeneous (single) as the mind would desire in its first transport of rapid generalisation is strengthened from year to year.

²⁸ The weakest point in the idea of elements is the negative character of the determinative signs given them by Lavoisier, and from that time ruling in chemistry. They do

The quantity, therefore, of each element remains constant in all chemical changes ; a fact which may be deduced as a consequence of the law of the indestructibility of matter, and of the conception of the elements themselves. Thus the equation expressing the law of the indestructibility of matter acquires a new and still more important signification. If we know the quantities of the elements occurring in the reacting substances which yield, by means of chemical changes, a series of new compound substances, then the latter will together contain the same quantity of each of the elements as originally existed in the reacting substances. The essence of chemical change is embraced in the study of how and with what each element is combined before and after change.

In order to be able to express chemical changes by equations, it has been agreed to represent each element by the first or some two letters of its (Latin) name. Thus, for example, oxygen is represented by the letter O ; nitrogen by N ; mercury (hydrargyrum) by Hg ; iron (ferrum) by Fe ; and so on for all the elements, as is seen in the tables given later on. A compound substance is represented by placing side by side the symbols representing the elements of which it is made up. For example, red mercury oxide is represented by HgO , which shows that it is composed of oxygen and mercury. Besides this, the symbol of every element corresponds with a certain relative quantity of it by weight, called its ' combining ' weight, or the weight of an atom ; so that the chemical formula of a compound substance designates not only the nature of the elements of which it is composed, but also their quantitative proportion. Every chemical process may be expressed by an equation composed of the formulæ corresponding with the reacting and resulting substances. The amount by weight of each element in a chemical equation must be the same on either side of the equation, since no element is either formed or destroyed in a chemical change.

On pages 24 and 25 is given a list of the elements and their symbols; while the preface contains a table of the elements, with their combining or atomic weights, and we shall see later, on what basis the atomic weights are determined. At present we will only point out that a compound containing the elements A and B is designated by the formula $A_n B_m$, where m and n are the coefficients or multiples in which the combining weights of the elements enter into the composition of

not decompose, they do *not change* into one another. But it must be remarked that elements form the limiting horizon of our knowledge of matter, and it is always difficult to determine a positive side on the borderland of what is known. However, there is no doubt (from the results of spectrum analysis) that the elements are distributed as far as the most distant stars, and that they support the highest attainable temperatures without decomposing.

the substance. If we represent the combining weight of the substance A by a , and that of the substance B by b , then the composition of the substance A_nB_m will be expressed thus: it contains na parts by weight of the substance A and mb of B, and consequently 100 parts of our compound contain $\frac{na}{na+mb} 100$ parts by weight of the substance A and $\frac{mb}{na+mb} 100$ of the substance B. It is evident that, as a formula shows the relative amounts of all the elements contained in a compound, the actual weights of the elements contained in a given weight of the compound may be calculated from its formula. For example, the formula of table salt, NaCl, shows (since Na=23 and Cl=35.5) that 100 parts of it contain 39.3 parts of sodium and 60.7 of chlorine.

What has been said above clearly limits the range of chemical changes, because from substances of a given kind there can be obtained only such as contain the same elements. Even with this limitation, however, the number of possible combinations is infinitely great. Only a comparatively small number of compounds have yet been described or subjected to research, and anyone working in this direction may easily discover new compounds which have not before been obtained. It often happens, however, that such newly discovered compounds were foreseen by chemistry, whose object is the apprehension of that uniformity which rules over the multitude of compound substances, and the comprehension of the laws which govern their formation and properties. The conception of elements having been established, the next objects of chemistry were the determination of the properties of compound substances on the basis of the quantity and nature of the elements of which they are composed; the investigation of the elements themselves; the determination of the compound substances which can be formed from each element and the properties exhibited by these compounds; and the apprehension of the nature of the connection between the elements in the different compounds. An element thus serves as the starting-point, being taken as the primary conception on which all other substances are built up.

When we state that a certain element enters into the composition of a given compound (when we say, for instance, that mercury oxide contains oxygen), we do not mean that it contains oxygen as a gaseous substance, but only desire to express those transformations which mercury oxide is capable of undergoing; that is, we wish to say that it is possible to obtain mercury and oxygen from mercury oxide, and that it can give up oxygen to various other substances; in a word, we desire only to give expression to those transformations of which mercury oxide

is capable. Or, more concisely, it may be said that the **composition** of a compound is the expression of those transformations of which it is capable. It is useful in this sense to make a clear distinction between the conception of an element as a *separate* homogeneous *substance* and as a *material part* or *element* of a compound. Mercury oxide does not contain two simple bodies, a gas and a metal, but two elements, mercury and oxygen, which, when free, are a gas and a metal. Neither mercury as a metal nor oxygen as a gas is present in mercury oxide, which only contains the substance of these elements, just as steam only contains the substance of ice, but not ice itself; or as bread contains the substance of the corn, but not the corn itself. The existence of an element may be recognised without knowing it in the uncombined state by merely investigating its combinations, and by the knowledge that it gives, under all possible conditions, substances which are unlike other known combinations of substances. Fluorine is an example of this kind. It was for a long time unknown in the free state, but nevertheless was recognised as an element because its combinations with other elements were known, and their difference from all other similar compound substances was determined. In order to grasp the difference between the conceptions of the visible form of an element as we know it in the free state and of the intrinsic **element** (or 'radicle,' as Lavoisier called it), it should be remarked that compound substances also combine together, forming yet more complex compounds. The original compound may often be extracted from these new compounds by exactly those methods by which elements are extracted from their corresponding combinations. Further, many elements exist under various visible forms, whilst the intrinsic element contained in these various forms is something which is not subject to change. Thus carbon appears as charcoal, graphite, and diamond, but yet the element carbon, of which each consists, is one and the same. Carbonic anhydride contains carbon, and not charcoal, or graphite, or the diamond.

Many elements, although not all of them, have the peculiar lustre, opacity, malleability, and the high thermal and electrical conductivities peculiar to the metals and their mutual combinations known as alloys. But elements are far from all being **metals**. Those which do not possess the physical properties of metals are called **non-metals**. These two classes of elements are clearly distinguished in certain definite examples, but in some cases the distinction is not clear, and hence cannot serve as a basis for the exact division of the elements into two groups.

The conception of elements forms the basis of chemical knowledge,

and in giving a list of them at the very beginning of our work we wish to tabulate our present knowledge on the subject. Altogether about 80 elements are now authentically known, some of them—about six—are so rarely met with in nature, and have been obtained in such small quantities, that we possess but a very insufficient knowledge of them. The substances most widely distributed in nature contain a very small number of elements, and these have been more completely studied than the others, because a greater number of investigators have been able to make experiments and observations on them. The elements most widely distributed in nature are:—

Hydrogen,	H.	In water, and in animal and vegetable organisms.
Carbon,	C.	In organisms, coal, limestones.
Nitrogen,	N.	In air and in organisms.
Oxygen,	O.	In air, water, earth. It forms the greater part of the mass of the earth.
Sodium,	Na.	In common salt and in many minerals.
Magnesium,	Mg.	In sea-water and in many minerals.
Aluminium,	Al.	In minerals and clay.
Silicon,	Si.	In sand, minerals, and clay.
Phosphorus,	P.	In bones, ashes of plants, and soil.
Sulphur,	S.	In pyrites, gypsum, and in sea-water.
Chlorine,	Cl.	In common salt and in sea-water.
Potassium,	K.	In minerals, ashes of plants, and in nitre.
Calcium,	Ca.	In limestones, gypsum, and in organisms.
Iron	Fe.	In the earth, iron ores, and in organisms.

Besides these, the following elements, although not very largely distributed in nature, are all more or less well known from their applications to the requirements of everyday life or the arts, either in the free state or as compounds:—

Lithium	Li.	In medicine (Li_2CO_3), and in photography (LiBr).
Boron	B.	As borax, $\text{B}_4\text{Na}_2\text{O}_7$, and as boric acid, BH_3O_3 .
Fluorine,	F.	As fluor spar, CaF_2 , and as hydrofluoric acid, HF .
Chromium,	Cr.	As chromic anhydride, CrO_3 , and potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$.
Manganese,	Mn.	As manganese peroxide, MnO_2 , and potassium permanganate, MnKO_4 .
Cobalt,	Co.	In smalt and blue glass.
Nickel,	Ni.	For electro-plating other metals.
Copper,	Cu.	The well-known red metal.
Zinc,	Zn.	Used for the plates of batteries; in brass, &c.

Arsenic,	As.	White arsenic (poison), As_2O_3 .
Bromine,	Br.	A brown volatile liquid ; sodium bromide, NaBr .
Strontium,	Sr.	In coloured fires (SrN_2O_6).
Silver,	Ag.	The well-known white metal.
Cadmium,	Cd.	White metal. Yellow paint (CdS).
Tin,	Sn.	The well-known metal.
Antimony,	Sb.	In alloys such as type metal.
Iodine,	I.	In medicine and photography ; free, and as KI .
Barium,	Ba.	'Permanent white,' and as an adulterant in white lead, and in heavy spar, BaSO_4 .
Platinum,	Pt.	} Well-known metals.
Gold,	Au.	
Mercury,	Hg.	
Lead,	Pb.	
Bismuth,	Bi.	In medicine and fusible alloys.

The compounds of the following elements have fewer applications, but are well known, and are fairly frequently met with in nature, although in small quantities :—

Beryllium,	Be.	Palladium,	Pd.	Titanium,	Ti.
Cerium,	Ce.	Vanadium,	V.	Tungsten,	W.
Selenium,	Se.	Osmium,	Os.	Zirconium,	Zr.
Iridium,	Ir.	Molybdenum,	Mo.	Thallium,	Tl.
Thorium,	Th.	Uranium,	U.		

The compounds of the following elements are still more seldom met with in nature. They have no applications, but have been studied somewhat fully :—

Scandium,	Sc.	Germanium,	Ge.	Gallium,	Ga.
Rubidium,	Rb.	Yttrium,	Y.	Cæsium,	Cs.
Niobium,	Nb.	Lanthanum,	La.	Ruthenium,	Ru.
Neodymium,	Nd.	Praseodymium,	Pr.	Samarium,	Sm.
Rhodium,	Rh.	Ytterbium,	Yb.	Indium,	In.
Tantalum,	Ta.	Tellurium,	Te.	Erbium,	Er.

Then a special group is formed by those gaseous substances discovered by Ramsay which enter in small quantities into the composition of air, and differ from all others in that they, so far, have given no compounds with other elements ; Helium, He ; Neon, Ne ; Argon, Ar ; Krypton, Kr ; and Xenon, Xe . There are also grounds for recognising the individuality of the metals : Actinium, Polonium, and Radium (discovered by Madame Curie), which enter into the composition of

the so-called radio-active compounds, occurring in small quantities in the native compounds of Uranium and Thorium.

Besides these 77 elements may be enumerated:—Gadolinium, Terbium, Thulium, Holmium, Karolinium, and several others. But owing to their extreme rarity, their properties and combinations are very little known, and even the existence of some of them as independent substances ²⁹ is doubtful.

It has been incontestably proved, from observations on the spectra of the heavenly bodies, that many of the commoner elements (such as H, Na, Mg, Fe) occur on the far-distant stars. This fact confirms the belief that those forms of matter which appear on the earth as elements are widely distributed throughout the entire universe. But we do not yet know why the mass of some elements in nature should be greater than that of others.^{29a}

The capacity of an element to combine with other elements, and to form with them more or less stable compounds which are in a greater or less degree prone to give new and yet more complex substances, forms the fundamental character of that element. Thus sulphur combines readily with the metals, oxygen, chlorine, or carbon, whilst gold and silver enter into combination with difficulty, and form unstable compounds, which are easily decomposed by heat. We must now consider the cause or force which induces the elements to enter into chemical change, and also that which holds different substances in combination—that is, which endows the substances formed with their particular degree of stability. This cause or force is called **affinity** (*affinitas*, *affinité*, *Verwandtschaft*), or chemical affinity.³⁰ Since this force must be regarded exclusively as an attractive force like gravity, many writers (for instance, Bergmann at the end of the eighteenth, and Berthollet at the beginning of the nineteenth century) supposed affinity

²⁹ There can be no mention of such contestable and doubtful elements in a short general handbook of chemistry.

^{29a} Clark in America made an approximate calculation of the amounts of the different elements contained in the earth's crust (to a depth of 15 kilometres), and found that the chief mass (about 50 per cent.) is composed of oxygen; then come silicon (about 25 per cent.), Al, Fe, &c., while the amount of hydrogen is less than 1 per cent., carbon scarcely 0·21 per cent., nitrogen even less than 0·03 per cent. The relative masses of such metals as Cu, Ni, and Au are very minute. Judging from the density (see Chapter VIII.) of the earth, a large proportion of its mass must be composed of iron.

³⁰ This word, first introduced into chemistry, if I mistake not, by Glauber, is based on the idea of the ancient philosophers that combination can only take place when the substances combining have something in common. As is generally the case, another idea evolved itself in antiquity, and has lived until now, side by side with the first, to which it is exactly contradictory: this considers union as dependent on contrast, on polar difference, on an effort to fulfil a want.

to be essentially similar to the universal force of gravity, from which it only differs in that the latter acts at observable distances, whilst affinity only evinces itself at the smallest possible distances. But chemical affinity cannot be entirely identified with the universal attraction of gravity, for the latter is dependent only on mass and distance, and not on the quality of the material acting, whilst it is by the quality of matter that affinity is most forcibly influenced. Neither can it be entirely identified with cohesion, which gives to homogeneous solid substances their crystalline form, elasticity, hardness, ductility, and other properties, and to liquids their surface tension, drop formation, capillarity, and other properties, because affinity acts between the component parts of a substance and cohesion on a substance in its homogeneity, although both these forces act at imperceptible distances (by contact) and have much in common. Nor can chemical force, which makes one substance penetrate into another, be entirely identified even with those attracting forces which make different substances adhere to each other or hold together (as when two plane-polished surfaces of solid substances are brought into close contact), or which cause liquids to soak into solids or adhere to their surfaces, or gases and vapours to condense on the surfaces of solids. These forces must not be confounded with chemical forces, which cause one substance to penetrate into the substance of another and form a new substance, which is never the case with cohesion. But it is evident that the forces which determine cohesion form a connecting-link between mechanical and chemical forces, because they only act by intimate contact. For a long time, and especially during the first half of the nineteenth century, chemical attraction and chemical forces were identified with electrical forces. There is certainly an intimate relation between them, for electricity is evolved in chemical reactions, and has also a powerful influence on chemical processes—for instance, compounds are decomposed by the action of an electric current. And the exactly similar relation which exists between chemical phenomena and the phenomena of heat (heat being developed by chemical phenomena, and being able also to decompose compounds) only proves the unity of the forces of nature, the capability of one force to produce and to be transformed into others. But for this reason the identification of chemical force with electricity will not bear experimental proof.³¹ As of all the (molecular) phenomena

³¹ Especially conclusive are those cases of so-called metalepsis (Dumas, Chapter II.). Chlorine, in combining with hydrogen, forms a very stable substance called 'hydrochloric acid,' which is split up by the action of an electric current into chlorine and hydrogen, the chlorine appearing at the positive and the hydrogen at the negative pole. Hence electro-chemists considered hydrogen to be an electro-positive and chlorine an electro-negative element, the two being held together by virtue of their opposite electrical charges.

of nature those of heat are at present the best (comparatively) known, having been reduced to the simplest fundamental principles of mechanics (of energy, equilibrium, and movement), which since Newton have been subjected to strict mathematical analysis, it is quite natural that an effort, which has been particularly pronounced during the last ten years, should have been made to bring chemical phenomena into strict correlation with the already investigated phenomena of heat, without, however, aiming at any identification of chemical with thermal phenomena. The true nature of chemical force is still a secret to us, just as is the nature of the universal force of gravity; and yet, without knowing what gravity really is, by applying mechanical conceptions, astronomical phenomena have not only been subjected to exact generalisation, but have also been employed for the detailed prediction of a number of particular facts; and so, also, although the true nature of chemical affinity may be unknown, there is reason to hope for considerable progress in chemical science by applying to it the laws of the mechanical theory of heat. As yet this portion of chemistry has not been fully worked out, and therefore, while forming a current problem of the science, it is treated more fully in a particular branch which is termed either 'theoretical' or 'physical' chemistry, or, more correctly, *chemical mechanics*. As this province of chemistry requires a knowledge, not only of the various homogeneous substances which have as yet been obtained and of the chemical transformations which they undergo, but also of the phenomena (thermal and other kinds) by which these transformations are accompanied, it is only possible to enter on the study of chemical mechanics after becoming acquainted with the fundamental chemical conceptions and substances which form the subject of this book.³²

It appears, however, from *metalepsis* that chlorine can replace hydrogen (and, inversely, hydrogen can replace chlorine) without in any way either changing the grouping of the other elements in a compound or altering its chief chemical properties. For instance, acetic acid in which hydrogen has been replaced by chlorine is still capable of forming salts. It must be observed, while considering this subject, that the explanation suggesting electricity as the origin of chemical phenomena is unsound, since it attempts to explain one class of phenomena whose nature is almost unknown by another class which is no better known. It is most instructive to remark that together with the electrical theory of chemical attraction there arose and still survives a view which explains the galvanic current as being a transference of chemical action through the circuit—i.e. regards the origin of electricity as a chemical one. It is evident that the connection is very intimate, although the two phenomena are independent and represent different forms of molecular (atomic) motion, whose real nature is not yet understood. Nevertheless, the connection between the phenomena of both categories is not only in itself very instructive, but it extends the applicability of the general idea of the unity of the forces of nature: conviction of the truth of which held so important a place in the science of the last decade.

³² I consider that in an elementary textbook of chemistry, like the present, it is only

As the chemical changes to which substances are liable proceed from internal forces peculiar to these substances, as chemical phenomena certainly consist of motions of material parts, and as the investigation of mechanical and physical phenomena proves the **law of the indestructibility of forces**, or conservation of energy, we are inevitably obliged to acknowledge in all substances (and especially in the elements) the presence of a store of **chemical energy** or invisible motion inducing them to enter into combinations. If heat is evolved in a reaction, it means that a portion of the chemical energy is transformed into heat;³³ if heat is absorbed in a reaction,³⁴ that it is partly transformed (rendered latent) into chemical energy. The store of force or energy which can be used for the formation of new compounds may, after several combinations accomplished with loss of heat, finally diminish to such a degree that indifferent compounds will be obtained, although these, by combining with energetic elements or compounds, give more complex compounds capable of entering into chemical combination. Among elements, gold, platinum, and nitrogen have but little energy, whilst potassium, oxygen, and chlorine possess it in a very marked degree. When dissimilar substances enter into combination they often form substances of diminished energy. Thus sulphur and potassium when heated readily burn in the air, but when combined together they yield a compound which is neither inflammable nor capable of burning in air like its component parts. Part of the energy

advisable, or even possible, to mention, in reference to chemical mechanics, a few general ideas and some particular examples referring more especially to gases and such equilibrated systems as are met with in dissociation and in the passage from one physical or chemical state to another. However, during recent times, owing mainly to the labours of van't Hoff and Gibbs, this province has expanded so largely that it forms a vast section of physical (theoretical) chemistry. The present work, in treating of the general principles of chemistry, and more particularly of the theory of the elements, can only serve as an introduction to such branches of our science as organic, analytical, physical, and technical chemistry.

³³ The theory of heat gave the idea of a store of internal motion or energy, and it therefore became necessary to recognise also chemical energy, but there is no foundation whatever for identifying thermal with chemical energy. It may be assumed, but not positively affirmed, that heat motion is peculiar to molecules and chemical motion to atoms, but as molecules are made up of atoms, the motion of the one passes to the other, and for this reason heat strongly influences chemical reactions during which it also appears or disappears (is absorbed). These relations, which are apparent and hardly subject to doubt on general lines, still present much that is doubtful in detail, because all forms of molecular and atomic motion are able to pass into each other.

³⁴ The reactions which take place (at ordinary or at high temperatures) directly between substances may be clearly divided into exothermal, which are accompanied by an evolution of heat, and endothermal, which are accompanied by an absorption of heat. It is evident that for the latter to take place a source of heat is necessary, and this is furnished either by the surrounding medium, by a secondary reaction proceeding simultaneously, or by some other form of energy.

of the potassium and sulphur was evolved during their combination in the form of heat. Just as in the passage of substances from one physical state to another a portion of their store of heat is absorbed or evolved, so in combinations or decompositions, and in all other chemical processes, there occurs a change in the store of chemical energy and at the same time an evolution or absorption of heat.

For the comprehension of chemical phenomena as mechanical processes—i.e. the study of the *modus operandi* of chemical phenomena—it is most important to consider (1) the facts gathered from *stoichiometry*, or that part of chemistry which treats of the quantitative relations, by weight or volume, of the reacting substances; (2) the distinction between the different forms and classes of chemical reactions; (3) the changes in properties produced by alteration in composition; (4) the phenomena which accompany chemical transformation; (5) a generalisation of the conditions under which reactions occur. As regards stoichiometry, this branch of chemistry has been worked out most thoroughly, and comprises laws (of Dalton, Avogadro-Gerhardt, and others) which bear so deeply on all parts of chemistry that at the present time the chief problem of chemical research consists in the application of general stoichiometrical laws to concrete examples. Even the very signification of reactions of combination, decomposition, and rearrangement, acquired, as we shall see, a new and special character under the influence of the progress of exact ideas concerning the quantitative relations of substances entering into chemical changes. Furthermore, in this sense there arose a new—and, till then, unknown—division of compound substances into **definite** and **indefinite compounds**. Even at the beginning of the nineteenth century Berthollet had not made this distinction. But Prout showed that many compounds contain the substances of which they are composed or into which they break up, in exact definite proportions by weight, which are unalterable under any conditions. Thus, for example, red mercury oxide always contains sixteen parts by weight of oxygen for every 200 parts by weight of mercury, and this relation is expressed by the formula HgO . But in an alloy of copper and silver one or the other metal may be added at will, and in an aqueous solution of sugar the relative proportions of the sugar and water may be altered and yet a homogeneous whole with the sum of the independent properties will be obtained—i.e., in these cases there is indefinite chemical combination. Although in nature and chemical practice the formation of indefinite compounds (such as alloys and solutions) plays as essential a part as the formation of definite chemical compounds, yet, as the stoichiometrical laws at present apply chiefly to the latter, all data

concerning indefinite compounds suffer from inexactitude, and it is only during recent years that the attention of chemists has been directed to this province of chemistry.^{34a}

In chemical mechanics it is very important to distinguish clearly between **reversible** and **non-reversible reactions**. Substances capable of reacting on each other at a certain temperature produce substances which at the same temperature either can or cannot give back the original substances. For example, salt dissolves in water at the ordinary temperature, and the solution so obtained is capable of breaking up at the same temperature, the water being separated by evaporation and salt left behind. Carbon bisulphide is formed from sulphur and carbon at the same temperature as that at which it can be resolved into sulphur and carbon. At a certain temperature iron separates hydrogen from water, forming iron oxide, which, in contact with hydrogen at the same temperature, is able to produce iron and water. It is evident that if two substances, A and B, give two others C and D, and the reaction be reversible (that is, C and D form A and B), then, by taking definite masses of A and B, or corresponding masses of C and D, we shall obtain, in either case, all four substances—that is to say, there will be a state of **chemical equilibrium** (or distribution) existing between the reacting substances. By increasing the mass of one of the substances we obtain a new condition of equilibrium, so that reversible reactions present a means of studying the **influence of mass** on the *modus operandi* of chemical changes. Many of those reactions which occur with very complicated compounds or mixtures may serve as examples of non-reversible reactions. Thus, many of the compound substances of animal and vegetable organisms

^{34a} The question of indefinite chemical compounds, particularly of solutions and alloys and their intimate connection with definite compounds, deeply interested me from the very beginning of my scientific career (in the fifties and sixties of the nineteenth century), when but slight attention was being paid to these matters. Several of my investigations had reference to such subjects (for instance, *Specific Volumes*, 1856; *The Compounds of Alcohol with Water*, 1865; *The Study of Aqueous Solutions*, 1887, &c.), which have therefore a special charm for me. But the *Principles of Chemistry*, which deals mainly with the elements and is a textbook for beginners, can only just touch the subject. Consequently I only consider solutions and alloys cursorily in passing, and chiefly in the notes, although since the publication of van't Hoff and Gibbs's work they have formed the object of extensive research. Their study occupies an important place in recent physical and theoretical chemistry, to which I refer my readers for further details. Moreover, I am of the opinion that the position of contemporary knowledge in the sphere of indefinite compounds has not the requisite completeness and generality for it to have much influence on the general principles of chemistry (although I am convinced that in time this will be accomplished), and therefore it will be best for the beginner to attack this subject after he has become acquainted with so-called general inorganic chemistry. I therefore refrain from burdening my book with a detailed discussion of my views on the subject.

are broken up by heat, but can at no temperature be re-formed from their products of decomposition. Gunpowder, as a mixture of sulphur, nitre, and carbon, on being exploded forms gas and a powdery smoke from which the original substance cannot be re-formed at any temperature. In order to obtain them, recourse must be had to an indirect method of **combination at the moment of separation**. If A does not under any circumstances combine directly with B, it does not follow that it cannot give a compound A B. For A can often combine with C, and B with D, and if C has a great affinity for D, then the action of A C on B D produces not only C D, but also A B. As, on the formation of C D, the substances A and B (previously in A C and B D) are left in a peculiar state of separation, it is supposed that their mutual combination occurs because they meet together in this **nascent state** (*in statu nascendi*). Thus chlorine does not directly combine with charcoal, graphite, or diamond; there are, nevertheless, compounds of chlorine with carbon, and many of them are distinguished by their stability. They are obtained in the action of chlorine on hydrocarbons, as the separation products from the direct action of chlorine on hydrogen. Chlorine takes up the hydrogen, and the carbon liberated at the moment of its separation enters into combination with another portion of the chlorine, so that in the end the chlorine is combined with both the hydrogen and the carbon.

As regards the phenomena accompanying chemical action, the most important circumstance in reference to chemical mechanics is that not only do chemical processes produce mechanical displacement (a motion of particles), heat, light, electrical potential and current, but that all these agents are themselves capable of changing and governing chemical transformations. This reciprocity or reversibility naturally depends on the fact that all the phenomena of nature are only different kinds and forms of visible and invisible (molecular) motions. First sound, and then light, were shown to consist of vibratory motions, as the laws of physics have proved and developed beyond a doubt. The connection of heat with mechanical motion and work has ceased to be a supposition, and has become an accepted fact, the mechanical equivalent of heat (425 kilogram-metres of mechanical work correspond with one kilogram unit of heat, or calorie) giving a mechanical measure for thermal phenomena. It is known that both statical and dynamical electricity are produced by mechanical means (e.g. in the dynamo machines of Gramme and others), and, conversely, a current (in electric motors) can produce mechanical motion. Thus by passing a current between the poles of a Gramme dynamo it may be made to revolve, and, conversely, by rotating it an electric current is produced, which

demonstrates the reversibility of electricity and mechanical motion. Accordingly chemical mechanics must look for the fundamental lines of its advancement in the correlation of chemical with physical and mechanical phenomena. But this subject, owing to its complexity and comparative novelty, has not yet been expressed by an harmonious theory, or even by a satisfactory hypothesis, and we shall therefore not linger over it, but leave this province of physical chemistry as a special branch of our science.

A chemical change in a certain direction is accomplished not only by reason of the difference of masses, the composition of the substances concerned, the distribution of their parts, and their affinity or chemical energy, but also by reason of the **conditions** under which the substances occur. In order that a certain chemical reaction may take place between substances capable of reacting on each other, it is often necessary to have recourse to conditions which are very different from those under which the substances usually occur in nature. For example, not only is the presence of air (oxygen) necessary for the combustion of charcoal, but the latter must also be heated to redness. The red-hot portion of the charcoal burns—i.e. combines with the oxygen of the atmosphere—and in so doing evolves heat, which raises the temperature of the adjacent parts of the charcoal, so that they burn. Just as the combustion of charcoal is dependent on its being heated to redness, so also every chemical reaction only takes place under certain physical, mechanical, or other conditions. The following are the chief conditions which exert an influence on the progress of chemical reactions.

(a) *Temperature*.—Chemical reactions of combination only take place within certain definite limits of temperature, and cannot be accomplished outside these limits. We may cite as examples that the combustion of charcoal begins only at a red heat, whilst chlorine or salt only combines with water at a temperature below 0°. These latter compounds cannot be formed at a higher temperature, for they are then wholly or partially broken up into their component parts. In certain cases of combination the effect of a rise of temperature may be explained as causing one of the reacting bodies to change from a solid into a liquid or gaseous form. This conversion into the fluid state facilitates the progress of the reaction, because it aids the intimate contact of the particles reacting on each other. Another cause, and to this must be ascribed the chief influence of heat in exciting chemical action, is that the physical cohesion, or the internal chemical union, of the homogeneous particles is thereby weakened, and in this way the separation of the particles of the original substances and their transference

into new compounds are rendered easier. When a reaction absorbs heat—as in decomposition—the reason why heat is necessary is self-evident.

At the present day it may be asserted, upon the basis of existing data respecting the action of high temperatures, that all compound bodies undergo decomposition at a more or less high temperature. We have already seen examples of this in describing the decomposition of mercury oxide into mercury and oxygen, and the decomposition of wood under the influence of heat. Many substances are decomposed at very moderate temperatures; for instance, the fulminating salt employed in cartridges is decomposed at a little above 120° . The majority of those compounds which constitute the mass of animal and vegetable tissues are decomposed at 200° . On the other hand, at very low temperatures, no reaction whatever can take place. Thus plants cease to carry on their chemical processes during the winter. Raoul Pictet (1892), employing the very low temperatures (as low as -200° C.) obtained by the evaporation of liquefied gases (see Chap. II.), has proved that at temperatures below -120° , even such reactions as those between sulphuric acid and caustic soda or metallic sodium do not take place, while the coloration of litmus by acids only commences at temperatures above -80° . Every chemical reaction requires a temperature between certain limits for its accomplishment, and there is no doubt that many of the chemical changes observed by us cannot take place in the sun, where the temperature is very high, or on the moon, where it is very low.

The influence of heat on reversible reactions is particularly instructive. If, for instance, a compound which is capable of being reproduced from its decomposition products be heated up to the temperature at which decomposition begins, the decomposition of a mass of the substance contained in a definite volume will not be immediately completed. Only a certain fraction of the substance is decomposed, the other portion remaining unchanged; and if the temperature be raised, the quantity of the substance decomposed will increase. Furthermore, for a given volume the ratio between the part decomposed and the part unaltered has a certain value for every definite temperature up to that at which the compound is entirely decomposed. This partial decomposition under the influence of heat is called **dissociation**. It is possible to distinguish between the temperatures at which dissociation begins and ends. Should dissociation proceed at a certain temperature, yet should the product or products of decomposition not remain in contact with the still undecomposed portion of the compound, then decomposition will go on to the end. Thus, in a lime-kiln, limestone is

completely decomposed into lime and carbonic anhydride, because the latter is carried off by the draught of the furnace. But if a certain mass of limestone be enclosed in a definite volume—for instance, in a gun-barrel in which it is sealed up—and heated to redness, then, as the carbonic anhydride cannot escape, only a certain proportion of the limestone will be decomposed at each definite temperature higher than that at which dissociation begins. Decomposition will cease when the carbonic anhydride evolved exerts a maximum *dissociation pressure* corresponding with each temperature. If the pressure be increased by increasing the quantity of gas, then combination begins afresh; if the pressure be diminished decomposition will recommence. Decomposition in this case is exactly similar to evaporation; if the steam given off by evaporation cannot escape, its pressure will reach a maximum corresponding with the given temperature, and then evaporation will cease. Should steam be added it will be condensed in the liquid; if its quantity be diminished—i.e. if the pressure be lessened, the temperature being constant—then evaporation will go on. We shall afterwards discuss more fully these phenomena of dissociation, which were first discovered by Henri St. Claire Deville. We will only remark that the products of decomposition recombine with greater facility the nearer their temperature is to that at which dissociation begins, or, in other words, that the initial temperature of dissociation is near to the initial temperature of combination. In certain instances chemical change proceeds at a fixed temperature which may be determined like (and compared to) the melting or boiling point. A given compound will decompose above this temperature, while below it combination or formation of the compound takes place. This may be observed, not only with the aid of a thermometer, but also by the rapid change of volume (by the dilatometer) which takes place at this *critical temperature*. Thus, gypsum or dihydrated calcium sulphate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) decomposes at 107° (in a closed vessel, otherwise the water escapes as steam) into a pasty liquid mass containing three-fourths of its water in a free state and hemi-hydrated calcium sulphate ($\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$). At lower temperatures the solid dihydrated salt is again formed.

(b) *The influence of an electric current*, and of electricity in general, on the progress of chemical transformations is very similar to the influence of heat. The majority of compounds which conduct electricity are decomposed by the action of a galvanic current, and as there is great similarity in the conditions under which decomposition and combination proceed, combination often proceeds under the influence of electricity. Electricity, like heat, must be regarded as a peculiar form of molecular motion, and all that refers to the influence of

heat also refers to the phenomena produced by the action of an electric current, only with this difference, that a substance can sometimes be separated into its component parts with much greater ease by electricity, since the process goes on at the ordinary temperature. The most stable compounds may be decomposed by this means, and a very important fact is then observed—namely, that the component parts appear at the different poles or electrodes by which the current passes through the substance. Those substances which appear at the positive pole (anode) are called ‘electro-negative,’ and those which appear at the negative pole (cathode) ‘electro-positive.’ The majority of non-metallic elements, such as chlorine, oxygen, &c., and also acids and substances analogous to them, belong to the first group, whilst the metals, hydrogen, and analogous products of decomposition or ions, appear at the negative pole. Chemistry is indebted to the decomposition of compounds by the electric current for many most important discoveries. Many elements have been discovered by this method, the most important being potassium and sodium. Lavoisier and the chemists of his time were not able to decompose the oxygen compounds of these metals, but Davy showed that they might be decomposed by an electric current, the metals sodium and potassium appearing at the negative pole. Now that the dynamo gives the possibility of producing an electric current by the combustion of fuel, by water power, &c., this method of Davy is advantageously employed for obtaining metals, &c., on a large scale ; for instance, sodium from fused caustic soda, or chlorine from solutions of salt.

(c) *The action of light* also decomposes certain unstable compounds. Photography is based on such a decomposition of certain substances (for instance, the salts of silver). The mechanical energy of those vibrations which determine the phenomena of light is very small, and therefore only certain generally unstable compounds can be decomposed by light—at least under ordinary circumstances. But there is one class of chemical phenomena dependent on the action of light which forms as yet an unsolved problem in chemistry—viz., the processes accomplished in plants under the influence of light. We find here the most varied decompositions and combinations, which are often unattainable by artificial means. For instance, carbonic anhydride, which is so stable towards the influence of heat and electricity, is nevertheless decomposed, and evolves oxygen in plants under the influence of light. Chlorine combines with hydrogen, under the influence, not only of heat, but also of light, which shows that combination, as well as decomposition, can be determined by its action.

(d) *Mechanical influences*, like the foregoing agents, exert an

action on the processes of both chemical combination and decomposition. Many substances are decomposed by friction or by a blow—as, for example, the compound called iodide of nitrogen (which is composed of iodine, nitrogen, and hydrogen) and silver fulminate. Mechanical friction causes sulphur to burn at the expense of the oxygen contained in potassium chlorate. Pressure affects both the physical and chemical states of the reacting substances, and, together with the temperature, determines the condition of a substance. This is particularly evident when the substance occurs in an elastic-gaseous form, since the volume and hence also the number of points of encounter between the reacting substances are greatly altered by a change of pressure. Thus, if the temperature be kept constant, hydrogen when compressed acts more powerfully upon iodine and on the solutions of many salts than at the ordinary pressure.

(e) The *influence of time* on the progress of chemical reactions is manifested, not only by the fact that the interpenetration of bodies, giving the possibility of their reacting together, requires a mechanical translation which can only proceed with a certain velocity (thus the combustion of a solid in air is determined by the removal from it and access to it, of air, and these actions only take place with a certain limited velocity), but also in the fact that after perfect contact has taken place the internal translation, determining chemical reactions, requires time, or proceeds at a certain rate. The ageing of wine is a well-known instance, a peculiar ‘bouquet’ or aromatic essences appearing in the wine after the course of time. These essences proceed from the acids and alcohol, present in the new wine in a free state, reacting together (a double decomposition), and in the course of time forming water and aromatic esters. This reaction, which proceeds slowly at the ordinary temperature, is one of the reversible reactions (i.e. an ester and water are able to give an alcohol and an acid), taking place with a distinctly limited velocity whose value depends upon the temperature and other conditions. There are many such retardative reactions, but the majority of the more distinct chemical changes (which should form the first object of study for the beginner) proceed so rapidly that the element of time is not, as a rule, taken into consideration in their investigation.³⁵

(f) The progress of chemical reactions is also accelerated or retarded by the *condition of contact* in which the reacting bodies occur. Other conditions remaining constant, the rate of progress of a chemical reaction is accelerated by increasing the number of points of contact.

³⁵ The rate of reaction is considered more fully in *Physical Chemistry*. In the present work it is only touched upon cursorily.

It will be enough to point out the fact that sulphuric acid does not absorb ethylene under ordinary conditions of contact, but only after continued shaking, by which means the number of points of contact is greatly increased. To ensure complete action between solids, it is necessary to reduce them to very fine powder and to mix them as thoroughly as possible. Spring, the Belgian chemist, has shown that finely powdered solids which do not react on each other at the ordinary temperature may, however, do so under an increased pressure. Thus, under a pressure of 6,000 atmospheres, sulphur combines with many metals at the ordinary temperature, and mixtures of the powders of many metals form alloys.^{35a} It is evident that an increase in the number of points or surfaces must be regarded as the chief cause producing reaction, which is doubtless accomplished in solids, as in liquids and gases, in virtue of an internal motion of the particles, which motion must exist, although in different degrees and forms, in all the states of matter. It is very important to direct attention to the fact that the internal motion or condition of the particles of matter must be different on the surface of a substance from what it is inside; because in the interior of a substance similar particles are acting on all sides of any particle, whilst at the surface they act on one side only. Therefore the condition of a substance at its surfaces of contact with other substances must be more or less modified by them—possibly in a manner similar to that caused by an elevation of temperature. These considerations throw some light on the action in the large class of **contact reactions**; that is, such as appear to proceed owing to the mere presence (contact, catalysis) of certain special substances. Porous or powdery substances are very prone to act in this way, especially spongy platinum and charcoal. For example, sulphurous anhydride does not combine directly with oxygen; but this reaction takes place in the presence of spongy platinum.³⁶

^{35a} Spring, in 1888, showed that a mixture of finely powered dry non-hygroscopic salts—acetate of sodium, $C_2H_3NaO_2$, and nitrate of potassium, KNO_3 —forms a hygroscopic mass, even under the ordinary atmospheric pressure (by simply lying in dry air), owing to the formation by substitution, of a new hygroscopic salt, acetate of potassium, $C_2H_3KO_2$, and nitrate of sodium, $NaNO_3$, thus proving that solids are capable of reacting on each other.

³⁶ Contact phenomena are considered in detail in the work of Professor Konovaloff (1884). In my opinion the state of the internal motions of the atoms in molecules is modified at the points of contact of substances, and this state determines chemical reactions, so that reactions of combination, decomposition, and rearrangement are accomplished by contact. Professor Konovaloff showed that a number of substances, under certain conditions of their surfaces, act by contact; for instance, finely divided silica (from the hydrate) acts just like platinum, decomposing certain compound ethers. As reactions only take place when the reacting substances are in close contact, it is probable that those modifications in the distribution of the atoms in molecules which

The above general and introductory chemical conceptions cannot be thoroughly grasped in their true sense without a knowledge of the detailed facts of chemistry to which we shall now turn our attention. It was, however, absolutely necessary on the very threshold to become acquainted with such fundamental principles as the laws of the indestructibility of matter and the conservation of energy; since it is only by their acceptance, and under their direction and influence, that the examination of particular facts can give practical and fruitful results.

come about by contact phenomena prepare the way for them. By this the rôle of contact phenomena is considerably extended. Such phenomena should explain the fact that a mixture of hydrogen and oxygen yields water (explodes) at different temperatures, according to the nature of the heated substance which transmits the temperature. In chemical mechanics, phenomena of this kind have great importance; but as yet they have been but little studied. It must not be forgotten that contact is a necessary condition for every chemical reaction.

CHAPTER I

ON WATER AND ITS COMPOUNDS

WATER is found almost everywhere in nature, and in all three physical states. As vapour, water occurs in the atmosphere over the entire surface of the earth. The vapour of water in condensing forms snow, rain, hail, dew, and fog. One cubic metre (or 1,000 litres, or 35·316 cubic feet) of air can contain at 0° only 4·8 grams of water, at 20° about 17·0 grams, and at 40° about 50·7 grams ; but ordinary air only contains about 60 per cent. of this amount. Air containing less than 40 per cent. of the possible amount of moisture is felt to be dry, whilst air which contains more than 80 per cent. is considered as distinctly damp.¹

¹ In practice the chemist has to deal continually with gases, and gases are often collected over water; in this case a certain amount of water passes into vapour which mixes with the gases. It is therefore most important that he should be able to calculate the amount of **moisture in air and other gases**. Let us imagine a cylinder standing in a mercury bath, and filled with a dry gas whose volume equals v , temperature t° , and pressure h mm. (h millimetres of a column of mercury at 0°). We will introduce water into the cylinder in such quantity that a small part remains in the liquid state, and consequently the gas becomes saturated with aqueous vapour; the volume of the gas will then increase (if a large quantity of water be taken, some of the gas will be dissolved in it, and the volume may therefore be diminished). We will further suppose that, after the addition of the water, the temperature remains constant; then the pressure and volume are increased. In order to investigate the phenomenon we will artificially increase the pressure and reduce the volume to the original volume v . Then the pressure will be greater than h , namely, $h+f$, which means that by the introduction of aqueous vapour the pressure of the gas is increased. The researches of Dalton, Gay-Lussac, and Regnault showed that this increase f is equal to the maximum possible pressure of aqueous vapour at the temperature at which the observation is made. The maximum pressure f for all temperatures may be found in the tables made from observations on the pressure of aqueous vapour. This may be expressed thus: The maximum pressure of aqueous vapour (and of all others) is the same, no matter whether the space containing it is a vacuum or filled with a gas. This rule is known as **Dalton's law**. Thus we have a volume of dry gas v , under a pressure h , and a volume of moist gas, saturated with vapour, under a pressure $h+f$. The volume v of the dry gas under a pressure $h+f$ occupies, from Boyle's law, a volume $\frac{vh}{h+f}$; consequently the volume occupied by the aqueous vapour under the pressure $h+f$ equals $v - \frac{vh}{h+f}$, or $\frac{vf}{h+f}$. Thus the volumes of the dry gas and of the moisture which occurs in it, at a pressure $h+f$, are in the ratio $f:h$; and, therefore, if the aqueous vapour

Water in the liquid state, falling as rain and snow, soaks into the soil, and collects together into springs, lakes, rivers, seas, and oceans.

saturates a space at a pressure H , the volumes of the dry air and of the moisture which is contained in it are in the ratio $H-f : f$, where f is the pressure of the vapour according to the tables of vapour pressure. Thus, if a volume N of a gas saturated with moisture be measured at a pressure H , then the volume of the gas when dry will be equal to $N \frac{H-f}{H}$. We thus obtain the following practical rule: If a volume of a gas

saturated with aqueous vapour be measured at a pressure H mm., the volume of dry gas contained in it will be obtained by finding the volume corresponding with a pressure equal to H less the pressure due to the aqueous vapour at the temperature observed.

The preceding ratio gives the maximum quantity of water which can be held in a gas, and the degree of moisture shows what fraction of this maximum quantity occurs in any given case when the vapour does not saturate the space occupied by the gas. Thus, if it is required to measure the volume of a moist gas, it must be either thoroughly dried or quite saturated with moisture, or else the degree of moisture determined. The first and last methods are inconvenient, so that recourse is usually had to the second. For this purpose water is introduced into the cylinder holding the gas to be measured; it is left for a certain time so that the gas may become saturated, care being taken that a portion of the water remains in a liquid state; then the volume of the moist gas is determined, from which that of the dry gas may be calculated.

In order to find the **weight of the aqueous vapour** in a gas it is necessary to know the weight of a cubic measure at 0° and 760 mm. Knowing that one cubic centimetre of air under these conditions weighs 0.001293 gram, and that the density of aqueous vapour is 0.62, we find that one cubic centimetre of aqueous vapour at 0° and 760 mm. weighs 0.0008 gram, and at a temperature t° and pressure h the weight of 1 cubic centimetre will be $0.0008 \times \frac{h}{760} \times \frac{273}{273+t}$ gram. We already know that v volumes of a gas at a temperature t° and pressure h contain $v \times \frac{f}{h}$ volumes of aqueous vapour when saturated, so that the weight of the aqueous vapour held in v volumes of a gas will be

$$v \times 0.0008 \times \frac{f}{760} \times \frac{273}{273+t}.$$

Accordingly the weight of water which is contained in unit volume of a gas depends only on the temperature and not on the pressure (this is **Dalton's law**). From this it is clear that if the weight of the vapour, p , contained in a given volume of a gas be known, it is easy to determine the degree of moisture, $r = \frac{p}{v \times 0.0008} \times \frac{760}{t} \times \frac{273+t}{273}$. On this is founded the very exact determination of the degree of moisture of air from the weight of water contained in a given volume. It is easy to calculate from the preceding formula the number of grams, p , of water contained at any pressure in 1 cubic metre of a gas saturated with vapour at various temperatures; for instance, at 30° , $f = 31.5$; hence $p = 29.84$ grams.

The laws of Mariotte, Dalton, and Gay-Lussac, which are here applied to gases and vapours, are not perfectly exact, but are approximately true. In fact the pressure of aqueous vapour is slightly less in a gas than in a vacuum, and the weight of aqueous vapour held in a gas is slightly less than it should be according to Dalton's law, as was shown by the experiments of Regnault and others. The difference does not, however, exceed 5 per cent. of the total pressure of the vapours. This **decrement in vapour pressure** which occurs in the intermixture of vapours and gases, although small, indicates that there is then already, so to speak, a beginning of chemical change. The essence of the matter is that in this case there occurs, as on contact (see preceding

It is absorbed from the soil by the roots of plants, which when fresh contain from 40 to 80 per cent. of their weight of water. Animals contain about the same proportion of water. In a solid state, water appears as snow or ice, or in a state intermediate between these two, which is seen on mountains covered with perpetual snow. The water of rivers,²

footnote), an alteration in the motions of the atoms in the molecules, and therefore also a change in the motion of the molecules themselves.

In the uniform intermixture of air and other gases with aqueous vapour, and in the ability of water to pass into vapour and form a uniform mixture with air, we have an instance of a physical phenomenon which is analogous to chemical phenomena, and forms indeed a transition from the one class of phenomena to the other. Between water and dry air there exists a kind of affinity which obliges the water to saturate and mix with the air. But such a homogeneous mixture is formed (almost) independently of the nature of the gas into which evaporation takes place; even in a vacuum the phenomenon occurs in exactly the same way as in a gas, and therefore it is not the property of the gas, nor its relation to water, but the property of the water itself, which compels it to evaporate, so that in this case chemical affinity is not yet operative—or at least its action is not clearly pronounced. That it does, however, play a certain part is seen from the deviation from Dalton's law.

² In falling through **the atmosphere, water** dissolves the gases of the air, nitric acid, ammonia, organic compounds, salts of sodium, magnesium, and calcium, and mechanically washes out a mixture of dust and microbes suspended in the atmosphere. The amount of these and certain other constituents is very variable. Even between the beginning and end of the same rainfall a variation which is often very considerable may be remarked. Thus, for example, Bunsen found that rain collected at the beginning of a shower contained 3·7 grams of ammonia per cubic metre, whilst that collected at the end of the same shower contained only 0·64 gram. The water of the entire shower contained an average of 1·47 gram of ammonia per cubic metre. In the course of a year rain supplies an acre of ground with as much as 15 kilos of nitrogen in a combined form. Marchand found in one cubic metre of snow water 15·63, and in one cubic metre of rain water 10·07, grams of sodium sulphate. Angus Smith showed that after thirty hours' rainfall at Manchester the rain still contained 34·3 grams of salts per cubic metre. A considerable amount of organic matter, namely, 25 grams per cubic metre, has been found in rain water. The total amount of solid matter in rain water reaches 50 grams per cubic metre. Rain water generally contains very little carbonic acid, whilst in river water there is a considerable quantity of it. In considering the nourishment of plants it is necessary to keep in view the substances which are carried into the soil by rain.

River water contains from 50 to 1,600 parts by weight of salts in 1,000,000 parts. The amounts of solid matter per 1,000,000 parts by weight contained in the chief rivers are as follows:—The Don 124, the Loire 135, the St. Lawrence 170, the Rhone 182, the Dnieper 187, the Danube from 117 to 234, the Rhine from 158 to 317, the Seine from 190 to 432, the Thames at London from 400 to 450, in its upper parts 387, and in its lower parts up to 1,617, the Nile 1,580, and the Jordan 1,052. The Neva is characterised by the remarkably small amount of solid matter it contains. From the investigations of Prof. G. K. Trapp, a cubic metre of Neva water contains 32 grams of incombustible and 23 grams of organic matter, or altogether about 55 grams. This is one of the purest waters met with in a river. The large amount of impurities in river water, and especially of organic impurity produced by pollution with putrid matter, makes the water of many rivers unfit for use.

The chief part of the soluble substances in river water consists of calcium salts. A hundred parts of the solid residues contain the following amounts of calcium carbonate: from the water of the Loire 53, from the Thames about 50, the Elbe 55, the Vistula 65, the Danube 65, the Rhine from 55 to 75, the Seine 75, the Rhone from 82 to 94. The Neva contains 40 parts of calcium carbonate per 100 parts of saline matter. The considerable

springs, oceans and seas, lakes and wells, contains various substances in solution, mostly salts—that is, substances resembling common

amount of calcium carbonate which river water contains is very easily explained from the fact that water which contains carbonic acid in solution easily dissolves calcium carbonate, which occurs all over the earth. Besides calcium carbonate and sulphate, river water contains the chlorides and other salts of magnesium, sodium, potassium, aluminium, iron, and manganese. The presence of nitrates has been proved with certainty in almost all kinds of well-investigated river water. The quantity of calcium phosphate does not exceed 0.4 gram in the water of the Dnieper, and the Don does not contain more than 5 grams. The water of the Seine contains about 15 grams of nitrates, and that of the Rhone about 8 grams. The amount of ammonia is much less: thus in the water of the Rhine there is about 0.5 gram in June and 0.2 gram in October. The water of the Seine contains the same amount. This is less than in rain water. Notwithstanding this insignificant quantity, the water of the Rhine alone, which is not so very large a river, carries about 16 tons of ammonia into the ocean every day. The difference between the amounts of ammonia in rain and river water depends on the fact that the soil through which the rain water passes is able to retain the ammonia and also many other substances, such as phosphoric acid, potassium salts, &c.

The water of springs, rivers, wells, and in general of those places from which it is taken for drinking purposes, may be injurious to health if it contains much organic pollution, the more so as in such water the lower organisms (bacteria) may rapidly develop, and these organisms often serve as the carriers or causes of infectious diseases. For instance, certain pathogenic (disease-producing) bacteria are known to produce typhoid, the Siberian plague, and cholera. Thanks to the work of Pasteur, Metchnikoff, Koch, and many others, this province of research has made considerable progress. It is possible to investigate the number and properties of the germs in water. In *bacteriological researches* a gelatinous medium in which the germs can develop and multiply is prepared with gelatine and water, which has previously been heated several times, at intervals, to 100° (it is thus rendered sterile; that is to say, all the germs in it are killed). The water to be investigated is added to this prepared medium in a definite and small quantity (sometimes diluted with sterilised water to facilitate the calculation of the number of germs), protected from dust (which contains germs), and then left at rest until whole families of lower organisms are developed from the separate germs. These families (colonies) are visible to the naked eye (as spots), and may be counted; and by examining them under the microscope, and observing the number of organisms they produce, their significance may be determined. The majority of bacteria are harmless, but there are undoubtedly pathogenic kinds whose presence is one of the causes of malady and of the spread of certain diseases. The number of bacteria in 1 cubic centimetre of water sometimes attains the immense figures of hundreds of thousands and millions. Certain well, spring, and river waters contain very few bacteria, and are free from disease-producing bacteria under ordinary circumstances. By boiling water the bacteria in it are killed, and therefore boiled water is less harmful for drinking purposes than fresh water. The best kinds of water for drinking purposes do not contain more than 300 bacteria in a cubic centimetre.

The amount of the gases dissolved in river water is much more constant than that of its solid constituents. One litre, or 1,000 grams, of water contains 40 to 55 c.c. of gas measured at normal temperature and pressure. In winter the amount of gas is greater than in summer or autumn. Assuming that a litre contains 50 c.c. of gases, it may be admitted that these consist on an average of 20 vols. of nitrogen, 20 vols. of carbonic anhydride (proceeding in all likelihood from the soil and partly from the atmosphere), and 10 vols. of oxygen. If the total amount of gases be less, the constituent gases are still in about the same proportion; in most cases, however, carbonic anhydride predominates. The water of many deep and rapid rivers contains less carbonic anhydride, which shows that they have been rapidly formed from atmospheric water, and that they

table salt in their physical properties and chief chemical transformations.³ Further, the quantity and nature of these salts differ

have not succeeded during a long and slow course in absorbing a greater quantity of carbonic anhydride. Thus, for instance, the water of the Rhine, near Strassburg, according to Deville, contains 8 c.c. of carbonic anhydride, 16 c.c. of nitrogen, and 7 c.c. of oxygen per litre. From the researches of Prof. M. R. Kapoustin and his pupils, it appears that in determining the quality of a water for drinking purposes it is most important to investigate the composition of the dissolved gases, more especially as regards the oxygen present.

³ **Spring water** is formed from rain water percolating through the soil. Naturally a part of the rain water is evaporated directly from the surface of the earth and from the vegetation on it. It has been shown that out of 100 parts of water falling on the earth only 36 parts flow to the ocean; the remaining 64 are evaporated or percolate far underground. After flowing underground along some impervious strata, water comes out at the surface in many places as springs whose temperature is determined by the depth from which the water has flowed. Springs penetrating to a great depth may become considerably heated, and this is why hot mineral springs, with a temperature of 30° and higher, are often met with. When a spring water contains substances which endow it with a peculiar taste, and especially if these substances are such as are only found in minute quantities in river and other flowing waters, it is termed a **mineral water**. Many such waters are employed for medicinal purposes. Mineral waters are classed according to their composition into—(a) saline waters, which often contain a large amount of common salt; (b) alkaline waters, which contain sodium carbonate; (c) bitter waters, which contain magnesia; (d) chalybeate waters, which hold iron carbonate in solution; (e) aerated waters, which are rich in carbonic anhydride; (f) sulphuretted waters, which contain hydrogen sulphide. Sulphuretted waters may be recognised by their smell of rotten eggs, and by their giving a black precipitate with lead salts, and also by their tarnishing silver objects. Aerated waters, which contain an excess of carbonic anhydride, effervesce in the air, have a sharp taste, and redden litmus paper. Saline waters leave a large residue of soluble solid matter on evaporation, and have a salt taste. Chalybeate waters have an inky taste, and are coloured black by an infusion of galls; on being exposed to the air they usually give a brown precipitate. The character of a mineral water is generally a mixed one. In the table below, analyses are given of certain mineral springs which are valued for their medicinal properties. The quantity of the substances present in the water is expressed in millionths by weight.

—	Calcium salts	Sodium chloride	Sodium sulphate	Sodium carbonate	Potassium iodide and bromide	Other potassium salts	Iron carbonate	Magnesium salts	Silica	Carbonic anhydride	Sulphuretted hydrogen	Total solid contents
I.	1,928	—	152	—	—	24	—	448	152	1,300	80	2,609
II.	816	386	1,239	26	—	43	—	257	46	1,485	—	2,812
III.	1,085	1,430	1,105	—	4	90	—	187	65	1,326	11	3,950
IV.	343	3,783	16	3,431	—	14	—	251	112	2,883	—	7,950
V.	3,406	15,049	—	—	2	—	7	1,587	229	—	76	20,290
VI.	352	3,145	—	95	35	50	1	260	11	20	—	3,970
VII.	308	1,036	2,583	1,261	—	—	4	178	75	—	—	5,451
VIII.	1,726	9,480	—	—	40	120	26	208	40	—	—	11,790
IX.	551	2,040	1,150	999	—	1	30	209	50	2,740	—	4,070
X.	285	558	279	3,813	—	—	7	45	45	2,268	—	5,031
XI.	340	910	Iron and aluminium sulphates				{ 1,020 1,660	940	190	2,550 330	{ Sulphuric and hydro- chloric acids	

I. Sergieffsky, a sulphur water, Gov. of Samara (temp. 8° C.), analysis by Clause.
 II. Geléznovodskya water source No. 10, near Patigorsk, Caucasus (temp. 22·5°), analysis by Fritzsche. III. Aleksandroffsky, alkaline-sulphur spring, Patigorsk (temp. 46·5°),

in different waters. Everybody knows that there are salt, fresh, iron, and other waters. The presence of about $3\frac{1}{2}$ per cent. of salts renders sea water⁴ bitter to the taste and increases its specific gravity. Fresh water also contains salts, but only in a comparatively small quantity (not above 1 per cent.) Their presence may be easily proved by simply evaporating water. On evaporation the water passes away as vapour, whilst the salts are left behind. This is why a crust consisting of salts, previously in solution, is deposited on the insides of kettles, boilers, and other vessels in which water is boiled. Running water (rivers &c.) is charged with salts, owing to its being formed from the collection of rain water percolating through the soil. During this percolation the water dissolves certain parts of the soil. Thus water which filters or passes through saline or calcareous soils becomes charged with salts or calcium carbonate (chalk). Rain water and snow are much purer than river or spring water. Nevertheless, in passing through the atmosphere, rain and snow succeed in

average of analyses by Herman, Zinin, and Fritzsche. IV. Bougountouksky, alkaline spring No. 17, Essentoukah, Caucasus (temp. 21.6°), analysis by Fritzsche. V. Saline water, Staro-Russi, Gov. of Novgorod, analysis by Nelubin. VI. Water from artesian well at the factory of State papers, St. Petersburg, analysis by Struve. VII. Sprüdel, Carlsbad (temp. 83.7°), analysis by Berzelius. VIII. Kreuznach spring (Elisenquelle), Prussia (temp. 8.8°), analysis by Bauer. IX. Eau de Seltz, Nassau, analysis by Henry. X. Vichy water, France, analysis by Berthier and Puvy. XI. Paramo de Ruiz, Colombia, analysis by Levy. This water is distinguished by the amount of free acids present.

⁴ **Sea water** contains more non-volatile saline constituents than the common types of fresh water. This is explained by the fact that the waters flowing into the sea supply it with salts, and whilst a large quantity of vapour is given off from the surface of the sea the salts remain behind. Even the specific gravity of sea water differs considerably from that of pure water. It is generally about 1.02, but in this, and also in the amount of salts present, samples of sea water from different localities and from different depths present rather remarkable variations. It will be sufficient to point out that 1 cubic metre of water from the undermentioned localities contains the following quantity in grams of solid constituents:—Gulf of Venice, 19,122; Leghorn Harbour, 24,312; the Mediterranean, near Cetta, 37,665; the Atlantic Ocean, from 32,585 to 35,695; and the Pacific Ocean, from 34,708 to 35,233. In closed seas which do not communicate, or are in very distant communication, with the ocean, the difference is often still greater. Thus the Caspian Sea contains 6,300 grams; the Black Sea and Baltic, 17,700. Common salt forms the chief constituent of the saline matter of sea or ocean water; thus in 1 cubic metre of sea water there are 25,000–31,000 grams of common salt, 2,600–6,000 grams of magnesium chloride, 1,200–7,000 grams of magnesium sulphate, 1,500–6,000 grams of calcium sulphate, and 10–700 grams of potassium chloride. The small amount of the organic matter and of the salts of phosphoric acid in sea water is very remarkable. Sea water (the composition of which is partially discussed in Chapter X.) contains, in addition to salts of common occurrence, a certain and sometimes minute amount of the most varied elements, even gold and silver; and as the mass of water of the oceans is so enormous these ‘traces’ of rare substances amount to large quantities, so that it may be hoped that in time methods will be found to extract even gold from sea water, which by means of the rivers forms a vast reservoir for the numerous products of the changes taking place on the earth’s surface.

catching the dust held in it and in dissolving air, which is found in every water. When water is heated the dissolved gases of the atmosphere are partly disengaged, as bubbles, and, after long boiling, water is quite freed from these gases.

In general terms water is called pure when it is clear and free from insoluble particles held in suspension and visible to the naked eye, from which it may be freed by filtration through charcoal, sand, or porous (natural or artificial) stones, and when it possesses a clean fresh taste. It depends on the absence of any taste of decomposing organic matter, on the quantity of air⁵ and atmospheric gases in solution, and on the presence of mineral substances to the amount of about 300 grams per ton (or 1,000 kilograms per cubic metre, or, what is the same, 300 milligrams to a kilogram or a litre of water), and of not more than 100 grams of organic matter.⁶ Such water is suitable for drinking and

⁵ The taste of water is greatly dependent on the quantity of dissolved gases it contains. These gases are given off on boiling, and it is well known that, even when cooled, boiled water has, until it has absorbed gaseous substances from the atmosphere, quite a different taste from fresh water containing a considerable amount of gas. The dissolved gases, especially oxygen and carbonic anhydride, have an important influence on the health. The following instance is very instructive in this respect. The Grenelle artesian well at Paris when first opened supplied a water which had an injurious effect on men and animals. It appeared that this water did not contain oxygen, and was in general very poor in gases. As soon as it was made to fall in a cascade, by which it absorbed air, it proved quite fit for consumption. In long sea voyages fresh water is sometimes not taken at all, or only taken in a small quantity, because it spoils by keeping and becomes putrid, owing to the decomposition of the organic matter it contains. Fresh water may be obtained directly from sea water by distillation. The distilled water no longer contains sea salts, and is therefore fit for consumption, but it is very tasteless, and has the properties of boiled water. In order to render it palatable certain salts, which are usually present in fresh water, are added to it, and it is made to flow in thin streams exposed to the air in order that it may become saturated with the component parts of the atmosphere—that is, absorb gases.

⁶ **Hard water** is such as contains much mineral matter, and especially a large proportion of calcium salts. Such water, owing to the amount of lime it contains, does not form a lather with soap, prevents vegetables boiled in it from softening properly, and forms a large amount of incrustation on vessels in which it is boiled. When of a high degree of hardness it is injurious for drinking purposes, as is evident from the fact that in several large cities the death-rate has been found to decrease after introducing a soft water in place of a hard one. Water containing decomposed organic matter may be purified by means of Condylé's fluid (potassium permanganate). A solution of this substance, even if very dilute, is of a red colour; on adding it to a putrid water the permanganate oxidises and destroys the organic matter. It is added to water in such a quantity as to impart to it an almost imperceptible rose colour. It is especially salutary to add a small quantity of Condylé's fluid to impure water in times of epidemic.

The presence in water of 1 gram per litre, or 1,000 grams per cubic metre, of any substance whatsoever renders it unfit, and even injurious, for consumption, and this is so, no matter whether organic or mineral matter predominates. The presence of 1 per cent. of chlorides makes water quite salt, and produces thirst instead of assuaging it. A large amount of nitrates is only found in impure and usually injurious water, as they often indicate the presence of decomposing organic matter.

every practical application, but evidently it is not pure in a chemical sense. A **chemically pure water** is necessary not only for scientific purposes, as an independent substance having constant and definite properties, but also for many practical purposes—for instance, in photography and in the preparation of medicines—because many properties of substances in solution are changed by the impurities of natural waters. Water is usually purified by distillation, because the solid substances in solution are not transformed into vapours in this process, and any gases in solution are driven off during the boiling. Such **distilled** water is prepared by chemists and in laboratories by boiling water in closed metallic boilers or stills, and causing the steam produced to pass into a condenser—that is, through tubes (which should be made of tin, or, at all events, tinned, as water and its impurities do not act on tin) surrounded by cold water, and in which the steam, being cooled, condenses into water which is collected⁷ in a receiver. By standing exposed to the atmosphere, however, the water in time absorbs air, and dust carried in the air. Nevertheless, in distillation, water retains, besides air, a certain quantity of volatile impurities (mostly organic), and the walls of the distillation apparatus are partly

⁷ Distilled water may be prepared on a small scale in the laboratory in a glass retort (fig. 4) heated by a lamp. Fig. 4 illustrates the main parts of the usual glass laboratory

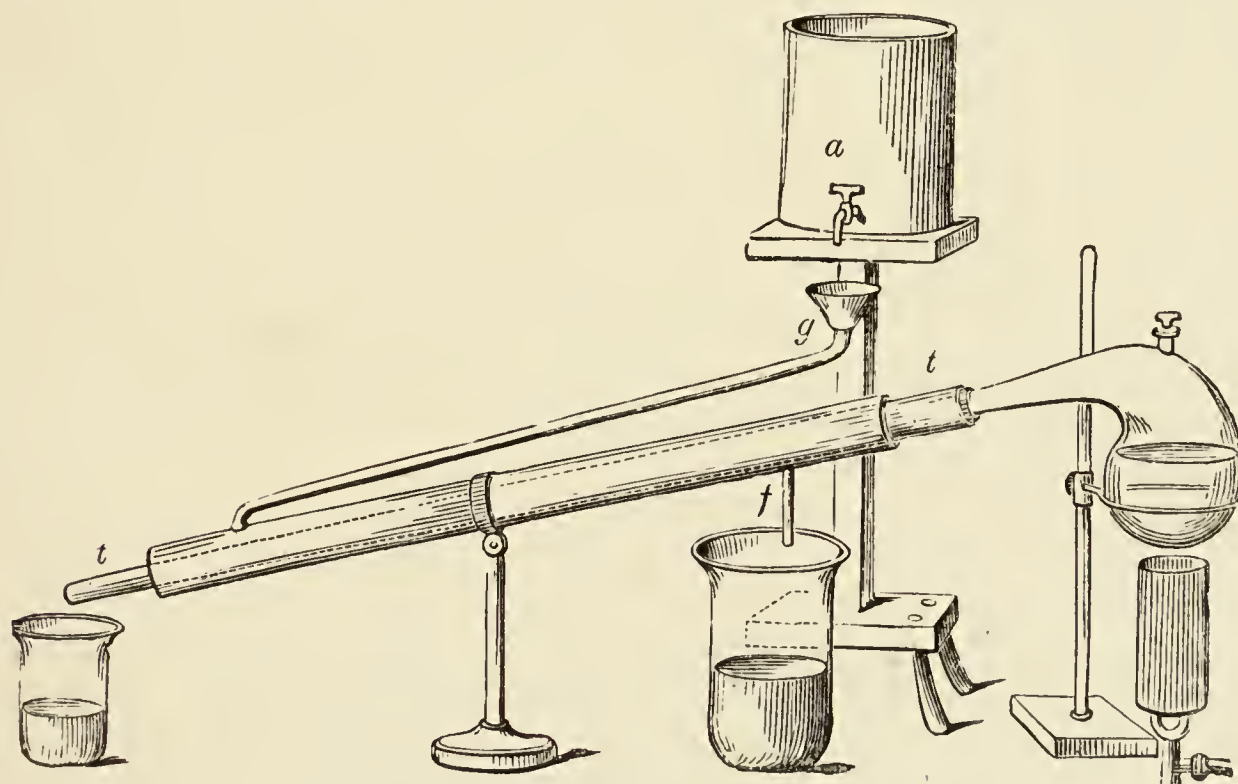


FIG. 4.—Distillation from a glass retort. The neck of the retort fits into the inner tube of the Liebig's condenser. The space between the inner and outer tubes of the condenser is filled with cold water, which enters by the tube *g* and flows out at *f*.

apparatus used for distillation. The steam issuing from the retort (on the right-hand side) passes through a glass tube surrounded by a larger tube, through which passes a stream of cold water, by which the steam is condensed and runs into a receiver (on the left-hand side).

corroded by the water, and a portion, although only a small one, of their substance renders the water not entirely pure, so that a residue is left on evaporation.⁸

For certain physical and chemical researches, however, it is necessary to have perfectly pure water. To obtain it, a solution of potassium permanganate is added to distilled water until the whole has a faint rose colour. By this means the organic matter in the water is destroyed (converted into gases or non-volatile substances). An excess of potassium permanganate does no harm, because in the next distillation it is left behind in the distillation apparatus. This second distillation should take place in a platinum retort with a platinum receiver. Platinum is a metal which is not acted on either by air or water, and therefore nothing passes from it into the water. The water obtained in the receiver still contains air. It must then be boiled for a long time, and afterwards cooled in a vacuum under the receiver of an air-pump, and must be kept in air-tight vessels. Pure water does not leave any residue on evaporation; does not in the least change, however long it is kept; does not decompose like water only once distilled or impure; and does not give bubbles of gas on heating, nor does it change the colour of a solution of potassium permanganate.

Water, purified as above described, has constant **physical and chemical properties**. For instance, it is of such water only that one cubic centimetre weighs one gram at 4° C.—i.e. it is only such pure water whose specific gravity equals 1 at 4° C.⁹ Water in a solid state

⁸ One of Lavoisier's first memoirs (1770) referred to this question. He investigated the formation of the earthy residue in the distillation of water in order to prove whether it was possible, as was affirmed, to convert water into earth, and he found that the residue was produced by the action of the water on the sides of the vessel containing it, and not from the water itself. He proved this to be the case by direct weighing.

⁹ Taking the generally accepted specific gravity of water at its greatest density—i.e. at 4°—as unity, it has been shown by experiment that the specific gravity of water at different temperatures is as follows:—

At	0°	.	.	.	0.99987	At	20°	.	.	.	0.99823
„	+ 10°	.	.	.	0.99973	„	30°	.	.	.	0.99568
„	15°	.	.	.	0.99913	„	100°	.	.	.	0.95859

A comparison of all the data at present known shows that the variation of the specific gravity S_t with the temperature t (determined by the hydrogen thermometer) may be expressed (Mendeléeff, 1896) between -5° and $+40^\circ$ C. by the formula

$$S_t = 1 - \frac{(t - 4)^2}{118932 + 1366.75t - 4.13t^2}.$$

If the temperature be determined by the mercurial thermometer, whose indications between 0° and 100° are slightly higher than those of the hydrogen thermometer (for example, about 0.1° C. at 20°), then a slightly higher sp. gr. will be obtained for a given t .

Water at 4° is taken as the basis for reducing measures of length to measures of weight and volume. The **metric or decimal system** of measuring weights and volumes is universally employed in science. The starting-point of this system is the metre (39.37

forms crystals of the hexagonal system,¹⁰ seen in snow, which generally consists of starlike clusters of several crystals, and also in the half-melted scattered ice floating on rivers in spring time. But ice also occurs, like many solids, in an amorphous (non-crystalline) form.

The temperatures at which water passes from one state to another are taken as fixed points on the thermometer scale; namely, the zero corresponds with the temperature of melting ice, and the temperature of the steam disengaged from water boiling at the normal barometric pressure (that is, 760 millimetres measured at 0°, at the latitude of 45°, at the sea level) is taken as 100° of the Celsius scale. Thus, the facts that ice liquefies at 0° and water boils at 100° are taken as characteristics of a definite chemical compound. The weight of a litre of water at 4° is 1,000 grams, and at 0°, 999.87 grams. The weight of a litre of ice at 0° is less—namely, 916 grams (according to Vincenna, 1902, the coefficient of cubical expansion of ice is 0.000152); the weight of the same cubic measure of water vapour at 760 mm. pressure and 100° is only 0.60 gram; the density of the vapour compared with that of air is 0.62, and compared with that of hydrogen, 9.

These data briefly characterise the physical properties of water as

inches) divided into decimetres (=0.1 metre), centimetres (=0.01 metre), millimetres (=0.001 metre), and microns (= one millionth of a metre). A cubic decimetre is called a **litre**, and is used for the measurement of volumes. The weight of a litre of water in a vacuum at 4° is called a kilogram. Platino-iridium standard samples of the **kilogram** and metre have been established by international treaty, and their prototypes have been distributed in many countries, with the object of establishing a uniformity of weights and measures. In Russia the law (1899) sanctions the use of the metric system on a par with the Russian by the mutual consent of the negotiating parties. The thousandth part of a kilogram weighs one **gram**. It is divided into decigrams, centigrams, and milligrams (=0.001 gram). An English pound equals 453.59 grams. The great advantage of this system is that it is a decimal one, and that it is universally adopted in science and in international relations. *All the measures cited in this work are metric.* The units most often used in science are:—Of length, the centimetre; of weight, the gram; of time, the second; of temperature, the degree Centigrade of the hydrogen thermometer.

According to the most trustworthy determinations the weight of a c. dcm. of water at 4° in vacuo is about 1 decigram less than a kilogram. For ordinary purposes the weight of a c. dcm. may be taken as equal to a kg. Hence the litre (or more truly the weight of water it holds) is equal to about 1000.1 cub. decimetres.

¹⁰ As solid substances appear in individual regular crystalline forms which are dependent, judging from their cleavage or lamination (in virtue of which mica breaks up into laminae, and Iceland spar, &c., into pieces bounded by faces inclined to each other at angles which are definite for each substance), on an inequality of attraction (cohesion elasticity) in different directions which intersect at definite angles, the determination of crystalline form affords one of the most important characteristics for identifying definite chemical compounds. The elements of crystallography, which is a special science, should therefore be familiar to all who desire to work in scientific chemistry. In this work we shall only have occasion to speak of a few crystalline forms, some of which are shown in figs. 5 to 11. But solids not only occur in crystalline forms determined by inequalities of cohesion and elasticity in different directions, by which (as also by their

a separate substance. To this may be added that water is a mobile liquid, colourless, transparent, without taste or smell, &c. Its latent

optical and electrical properties) they differ distinctly from liquids (which are of uniform structure in all directions, or isotropic), but also in an amorphous or isotropic state—without any difference of structure in different directions—which is best illustrated by

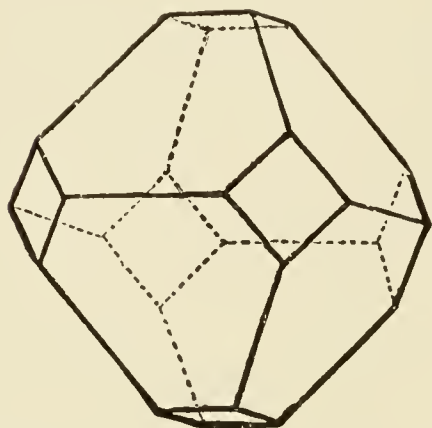


FIG. 5.—Example of the form belonging to the regular system. Combination of an octahedron and a cube. The former predominates. Alum, fluor spar, suboxide of copper, and others.

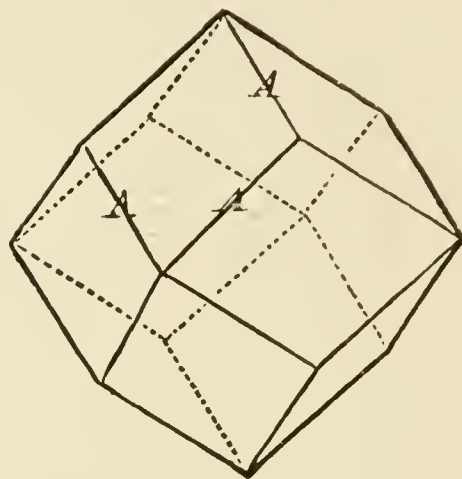


FIG. 6.—Rhombic dodecahedron of the regular system. Garnet.

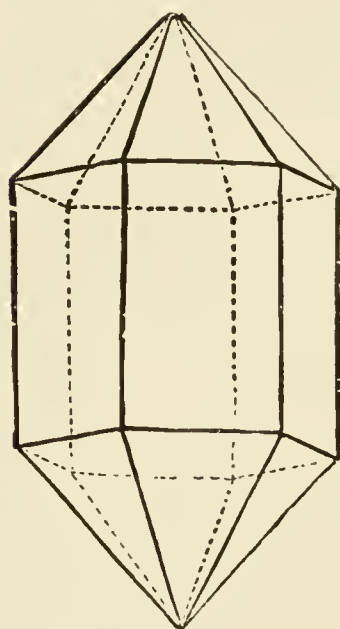


FIG. 7.—Hexagonal prism terminated by hexagonal pyramids. Quartz, &c.

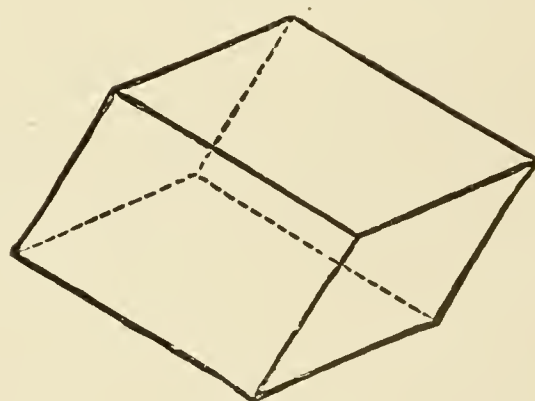


FIG. 8.—Rhombohedron. Calc spar, &c.

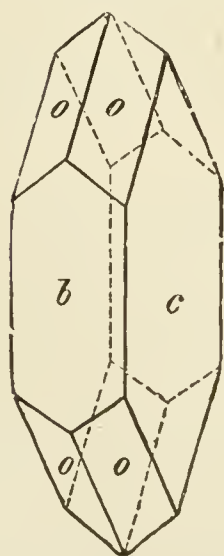


FIG. 9.—Rhombic system. Desmine.

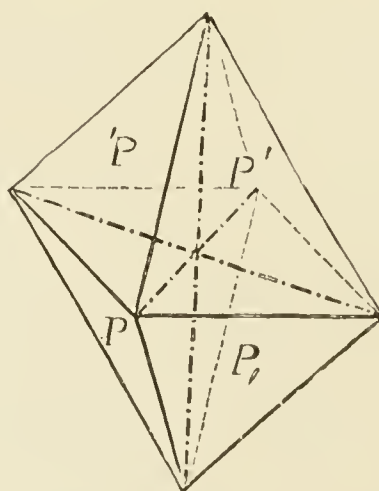


FIG. 10.—Triclinc pyramid.

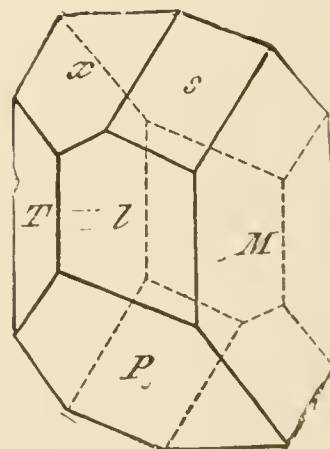


FIG. 11.—Triclinc system. Albite &c.

heat of vaporisation is 538 units, and that of liquefaction 79 units of heat.¹¹ The large amount of heat stored up in water vapour and also in

glass. When a solid forms by solidification from a liquid (i.e., from a molten state) it generally appears in an amorphous state, and only passes into a crystalline form by the agency of other bodies (especially crystals and such like substances) or under certain conditions of temperature and pressure. This subject, especially since Prof. Tamman's (Yurieff University, 1890–1902) recent researches, is of great interest, not only from a physico-mechanical, but also from a chemical point of view.

¹¹ Of all known liquids, water exhibits the greatest **cohesion** of particles. Indeed, it ascends in capillary tubes to a greater height than other liquids; for instance, two and a half times as high as alcohol, nearly three times as high as ether, and to a much greater height than oil of vitriol, &c. In a tube 1 mm. in radius, water at 0° ascends 15·3 mm., measuring from the height of the liquid to two-thirds of the height of the meniscus, and at 100° it rises 12·5 mm. The cohesion varies very uniformly with the temperature; thus at 50° the height of the capillary column equals 13·9 mm.—that is, the mean between the heights at 0° and 100°. This uniformity is not destroyed even at temperatures near the freezing-point, and hence it may be assumed that at high temperatures cohesion will vary as uniformly as at ordinary temperatures; so that at some temperature near 370° water should not ascend in a capillary tube. The cohesion between the particles of water would then be nil, and a peculiar critical state is attained of which mention will be made presently. Only certain solutions (sal-ammoniac and lithium chloride)—and these only with a great excess of water—rise higher than pure water in capillary tubes. The great cohesion of water doubtless determines many of both its physical and chemical properties.

The quantity of heat required to raise the temperature of one part by weight of water from 0° to 1°, i.e., by 1° C., is called the *unit of heat* or calorie; the **specific heat of liquid water** at 0° is taken as equal to unity. The variation of this specific heat with rise of temperature is inconsiderable in comparison with the variation exhibited by the specific heats of other liquids. The specific heat of water at 20° is 0·993, and at 100°, 1·073. The specific heat of water is greater than that of any other known liquid; for example, the specific heat of alcohol at 0° is 0·55—i.e., the quantity of heat which raises the temperature of 55 parts of water 1° raises that of 100 parts of alcohol 1°. The specific heat of oil of turpentine at 0° is 0·41, of ether 0·53, of acetic acid 0·5274, and of mercury 0·033. Hence water is the best condenser or absorber of heat. This property of water has an important significance in practice and in nature. Water prevents rapid cooling or heating, and thus tempers cold and heat. The specific heats of ice and aqueous vapour are much less than that of water, that of ice being 0·504, and that of steam 0·48.

With an increase in pressure equal to one atmosphere, the compressibility of water is 0·000047, of mercury 0·00000352, and of ether 0·00012 at 0°. The addition of various substances to water generally decreases both its compressibility and cohesion. The compressibility of other liquids increases with a rise of temperature, but for water it decreases up to 53° and then increases as with other liquids.

The **expansion of water** by heat (note 9) also exhibits many peculiarities which are not found in other liquids. The expansion of water at low temperatures is very small compared with that of other liquids: at 4° it is almost zero, and at 100° it is equal to 0·0008; below 4° it is negative—i.e., water on cooling does not then decrease in volume, but expands. In passing into the solid state, the specific gravity of water decreases; at 0° 1 c.c. of water weighs 0·99987 gram, and 1 c.c. of ice at the same temperature weighs only 0·916 gram. The ice formed, however, contracts on cooling like the majority of other substances. Thus 100 volumes of ice are produced from 92 volumes of water—that is, water expands considerably on freezing, which fact determines a number of natural phenomena. The freezing-point of water falls with an increase in pressure (0·007° per atmosphere), because water in freezing expands (Thomson), whilst with substances which contract in solidifying, the melting-point rises with an increase in

liquid water (for its specific heat is greater than that of other liquids)

pressure; thus, paraffin under one atmosphere melts at 46° , and under 100 atmospheres at 49° . The above proves that, under very considerable pressures, the densities of water and ice tend to become equal, and that a point may be reached where ice will sink under water. This has been confirmed by Tamman's researches (1890-1902) on the influence of temperature and pressure on the formation of amorphous and crystalline solids from liquids.

When liquid water passes into vapour the cohesion of its particles must be destroyed, as the particles are removed to such a distance from each other that their mutual attraction no longer exhibits any influence. As the cohesion of aqueous particles varies at different temperatures, the quantity of heat which is expended in overcoming this cohesion—or the **latent heat of evaporation**—will for this reason alone be different at different temperatures. The quantity of heat which is consumed in the transformation of one part by weight of water, at different temperatures, into vapour was determined with great accuracy by Regnault, Griffiths (1895), and others. It is found that one part by weight of water at 0° , in passing into vapour having a temperature t° , consumes $640 + (t - 100) 0.6$ units of heat; that is, at 100° , 640, and at 200° , 700 heat units. But this quantity includes also the quantity of heat required for heating the water from 0° to t° —i.e., besides the latent heat of evaporation, also that heat which is used in heating the water in a liquid state to a temperature t° . On deducting this amount of heat, we obtain the latent heat of evaporation of water as 598 at 0° , 538 at 100° , and 478 at 200° . From this we may conclude that at a certain temperature no heat would be required for the conversion of water into vapour. At this temperature, water passes into vapour, whatever be the pressure (see Chap. II. The absolute boiling-point of water is about 365°). It must here be remarked that water, in presenting a greater cohesion, requires a larger quantity of heat for its conversion into vapour than other liquids.

The whole amount of heat which is consumed in the conversion of water into vapour is not used in overcoming the cohesion—that is, in internal work accomplished in the liquid. A part of this heat is employed in moving the aqueous particles; in fact, aqueous vapour at 100° occupies a volume 1,650 times greater than that of water (at the ordinary pressure); consequently a portion of the heat or work is employed in lifting the aqueous particles, in overcoming pressure, or in external work, which may be usefully employed, and which is so employed in steam engines. In order to determine this work let us consider the variation of the maximum **vapour pressure of steam** at different temperatures. The observations of Regnault in this connection, as on those preceding, deserve special attention owing to their comprehensiveness and accuracy. The pressure of aqueous vapour at various temperatures is given in the subjoined table, and is expressed in millimetres of the barometric column reduced to 0° .

Temperature	Pressure	Temperature	Pressure
-20°	0.9	70°	233.3
-10°	2.1	90°	525.4
0°	4.6	100°	760.0
$+10^{\circ}$	9.1	105°	906.4
15°	12.7	110°	1075.4
20°	17.4	115°	1269.4
25°	23.5	120°	1491.3
30°	31.5	150°	3581.0
50°	92.0	200°	11689.0

This table shows the boiling-points of water at different pressures. Thus on the summit of Mont Blanc, where the average pressure is about 424 mm., water boils at 84.4° ; and at a pressure of five atmospheres (five times the ordinary atmospheric pressure—i.e., $5 \times 760 = 3,800$ mm.) the temperature of the water would be 152° . As a column of mercury 1 mm. high exerts a pressure of 13.596 grams on a

renders it available in both forms for heating purposes.¹² The chemical reactions which water undergoes, and by means of which it is formed,

surface of 1 sq. cm., the pressure of the atmosphere, 760 mm., corresponds with a pressure of 1033·28 grams per square centimetre. This means that if a cylinder be taken whose sectional area equals 1 sq. cm., and if water be poured into it and it be closed by a piston weighing 1,033 grams, then on heating it *in a vacuum* to 100° no steam will be formed, because the steam cannot overcome the pressure of the piston; and if at 100° 538 units of heat be transmitted to each unit of weight of water, then the whole of the water will be converted into vapour having the same temperature. The question now arises, to what height does the piston rise under these circumstances; that is, in other words, what is the volume occupied by the steam under a known pressure? For this we must know the weight of a cubic centimetre of steam at various temperatures. It has been shown by experiment that the density of steam, with reference to air at the same temperature and pressure, is 0·62. Steam which saturates a space varies in density at different temperatures, but this difference is very small, and its average density with reference to air is 0·64. Now one cubic centimetre of air at 0° and 760 mm. weighs 0·001293 gram, while at 100° and under the same pressure it will weigh $\frac{0·001293}{1·368}$ or

about 0·000946 gram, and consequently one cubic centimetre of steam whose density is 0·64 will weigh 0·000605 gram at 100°, and one gram of aqueous vapour will occupy a volume of about 1,653 c.c. Consequently the piston in the cylinder of 1 sq. cm. sectional area, and in which the water occupied a height of 1 cm., will be raised 1,653 cm. on the conversion of this water into steam. This piston, as has been mentioned, weighs 1,033 grams, therefore the **external work of the steam**—that is, that work which the water does in its conversion into steam at 100°—is equal to lifting a piston weighing 1,033 grams to a height of 1,653 cm., or 17·07 kilogram-metres of work—i.e., is capable of lifting 17 kilograms 1 metre, or 1 kilogram 17 metres. One gram of water requires for its conversion into steam 538 gram units of heat or 0·538 kilogram unit of heat—i.e., the quantity of heat absorbed in the evaporation of one gram of water is equal to the quantity of heat which is capable of heating 1 kilogram of water 0·538°. Each unit of heat, as has been shown by accurate experiment, is capable of doing 425 kilogram-metres of work. Hence, in evaporating, one gram of water expends $425 \times 0·538 =$ (almost) 227 kilogram-metres of work. The external work was found to be only 17 kilogram-metres; therefore 210 kilogram-metres are expended in overcoming the internal cohesion of the aqueous particles, and consequently about 92 per cent. of the total heat or work is consumed in overcoming the internal cohesion.

The work necessary for overcoming the internal cohesion of water in its passage into vapour decreases with the rise in temperature; that is, corresponds with the decrease of cohesion; and the variations which take place in this case are very similar to those which are observed in the heights to which water rises in capillary tubes at different temperatures. It is evident, therefore, that the amount of external—or, as it is termed, useful—work which water can supply by its evaporation is very small compared with the amount which it expends in its conversion into vapour.

It is evident from the above considerations that, even in a physical change of state, the greatest part of the work done is employed in overcoming cohesion, but an enormous amount of internal energy must be expended in overcoming chemical cohesion or affinity.

¹² When it is necessary to heat a considerable mass of liquid in different vessels, it would be very uneconomical to make use of metallic vessels and to construct a separate furnace for each. Such cases are continually met with in practice. Steam from a boiler is introduced into the liquid, or, in general, into the vessel which it is required to heat. The steam, in condensing and passing into a liquid state, parts with its latent heat; and as this is very considerable a small quantity of steam will produce a considerable heating effect. If it be required, for instance, to heat 1,000 kilos of water from 20° to 50°, which requires approximately 30,000 units of heat, steam at 100° is passed into the water

are so numerous, and so closely allied to the reactions of many other substances, that it is impossible to describe the majority of them at this early stage of chemical exposition. We shall become acquainted with many of them afterwards, but at present we shall only cite certain compounds formed by water. In order to see clearly the nature of the various kinds of compounds formed by water, we will begin with the most feeble, which are determined by purely mechanical superficial properties of the reacting substances.

Water is mechanically attracted by many substances: it adheres to their surfaces just as dust adheres to objects, or one piece of polished glass adheres to another. Such attraction is termed 'moistening,' 'soaking,' or 'absorption of water.' Thus water is absorbed by the soil, sand, and clay, and does not flow away from them, but lodges itself between their particles. Similarly, water soaks into a sponge, cloth, hair, or paper, &c.; but fat and greasy substances in general are not moistened. Attraction of this kind does not alter the physical or chemical properties of water. For instance, under these circumstances water, as is known from everyday experience, may be expelled from objects by drying. Water which is in any way held mechanically may be dislodged by mechanical means, by friction, pressure, centrifugal force, &c. Thus water is squeezed from wet cloth by pressure or centrifugal machines. But objects which in practice are called dry (because they do not feel wet) often still contain moisture, as may be proved by heating the object in a glass tube closed at one end. On placing a piece of paper, dry earth, or any similar object (especially porous substances) in such a glass tube, and heating that part of the tube where the object is situated, it will be remarked that water condenses on the cooler portions of the tube. The presence of such absorbed, or 'hygroscopic,' water is generally best detected in non-volatile substances by drying them either at 100° , or under the receiver of an air-pump and over substances which attract water chemically. By weighing a substance before and after drying, it is easy to determine the amount of hygroscopic water from the loss in weight.¹³ But in

from a boiler. Each kilogram of water at 50° contains about 50 units of heat, and each kilogram of steam at 100° contains 640 units of heat; therefore each kilogram of steam in cooling to 50° gives up 590 units of heat, and consequently 51 kilos of steam are capable of heating 1,000 kilos of water from 20° to 50° . Water is very often applied for heating in chemical practice. For this purpose metallic vessels or pans, called 'water-baths,' are made use of. They are closed by a cover formed of concentric rings lying on each other. The vessels—such as beakers, evaporating basins, retorts, &c.—containing liquids, are placed on these rings, and the water in the bath is heated. The steam given off heats the bottom of the vessels to be heated, and thus effects the evaporation or distillation.

¹³ In order to dry any substance at about 100° —that is, at the boiling-point of water

this case the amount of water must be judged with care, because the loss in weight may sometimes proceed from the decomposition of the

(hygroscopic water passes off at this temperature)—an apparatus called a 'drying-oven' is employed. It consists of a double copper box; water is poured into the space between the internal and external boxes, and the oven is then heated over a stove or by any other means, or else steam from a boiler is passed between the walls of the two boxes. When the water boils, the temperature inside the inner box will be approximately 100°C . The substance to be dried is placed inside the oven, and the door is closed. Several holes are cut in the door to allow the free passage of air, which carries off the aqueous vapour by the chimney on the top of the oven. Often, however, desiccation is carried on in copper ovens heated directly over a lamp (fig. 12). In this case any desired temperature may be obtained, and is determined by a thermometer fixed in a special orifice. In order to determine directly the amount of water in a substance which

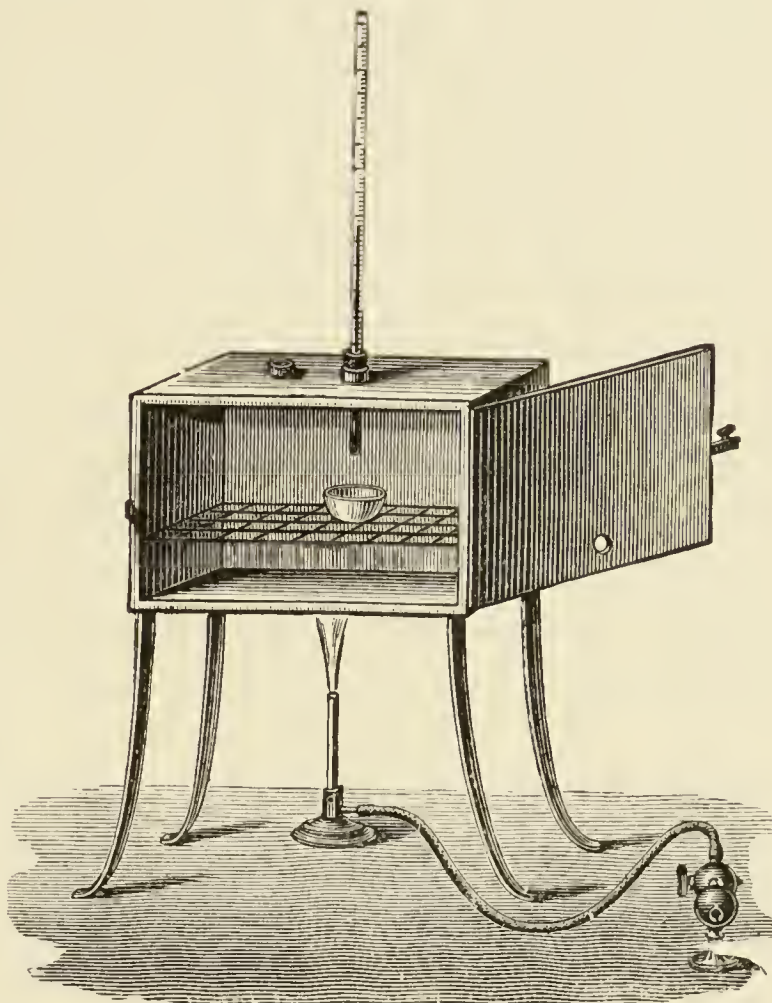


FIG. 12.—Drying oven, constructed of brazed copper. It is heated by a lamp. The object to be dried is placed on the gauze inside the oven. The thermometer indicates the temperature.

does not part with anything except water at a red heat, the substance is placed in a bulb tube. By first weighing the tube empty and then with the substance to be dried in it, the weight of the substance taken may be found. The tube is then connected on one side with a gas-holder full of air, which, on opening a stop-cock, passes first through a flask containing sulphuric acid, and then into a

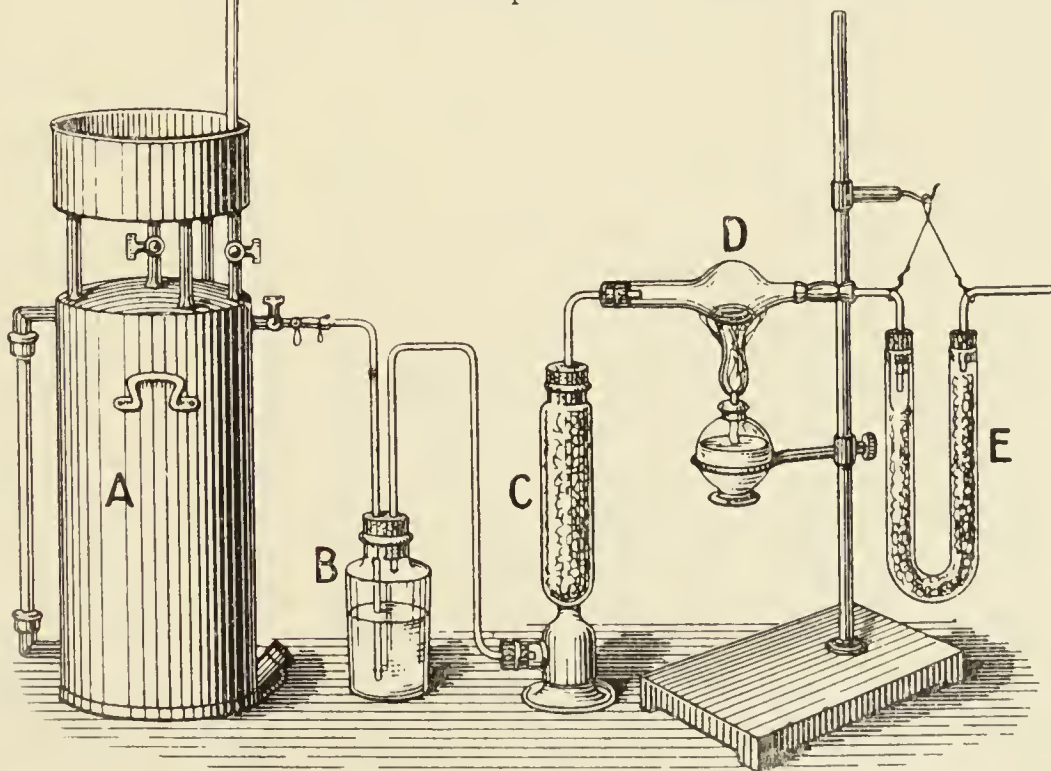


FIG. 13.—Determination of the quantity of water in a substance by heating it (in D) in a stream of air proceeding from A and dried in B and C; the water from the substance in D is collected in E and weighed.

vessel containing lumps of unice-stone moistened with sulphuric acid. In passing through these vessels

substance itself, with disengagement of gases or vapour. In making exact weighings the hygroscopic capacity of substances—that is, their capacity to absorb moisture—must be continually kept in view, as otherwise the weight will be untrue owing to the presence of moisture. The quantity of moisture absorbed depends on the degree of moisture of the atmosphere (that is, on the pressure of the aqueous vapour in it) in which a substance is situated. In a perfectly dry atmosphere, or in a vacuum, the hygroscopic water is expelled, being converted into vapour; therefore substances containing hygroscopic water may be completely dried by placing them in a dry atmosphere or in a vacuum. The process is aided by heat, which increases the pressure of the aqueous vapour. Phosphoric anhydride (a white powder), liquid sulphuric acid, solid and porous calcium chloride, and the white powder of ignited copper sulphate, are most generally employed in drying gases. They absorb the moisture contained in air and all gases to a considerable, but not unlimited, extent. Phosphoric anhydride and calcium chloride deliquesce, become damp, sulphuric acid changes from a thick oily liquid into a more mobile one, and ignited copper sulphate becomes blue; after which changes these substances partly lose their capacity of holding water, and can, if it be in excess, even give up their water to the atmosphere. We may remark that the order in which these substances are placed above corresponds with the order in which they stand in respect to their capacity for absorbing moisture. Air dried by calcium chloride still contains a certain amount of moisture, which it can give up to sulphuric acid. The most complete desiccation takes place with phosphoric anhydride. Water is also removed from many substances by placing them in a dish over a vessel containing a substance absorbing water under a glass bell jar.¹⁴

the air is thoroughly dried, having given up all its moisture to the sulphuric acid. Thus dry air will pass into the bulb tube. The moisture given up by the substance in the tube will be carried off by the air passing through it. This damp air then passes through a **U**-shaped tube full of pieces of pumice-stone moistened with sulphuric acid, which absorbs all the moisture given off from the substance in the bulb tube. Thus all the water expelled from the substance will collect in the **U**-tube; and so, if this be weighed before and after, the difference will show the quantity of water expelled from the substance. If only water (and no gases) come over, the increase of the weight of the **U**-tube will be equal to the decrease in the weight of the bulb tube.

¹⁴ Instead of under a glass bell jar, drying over sulphuric acid is often carried on in a desiccator consisting of a shallow wide-mouthed glass vessel, closed by a well-fitting ground-glass cover. Sulphuric acid is poured over the bottom of the desiccator, and the substance to be dried is placed on a glass stand above the acid. A lateral glass tube with a stop-cock is often fused into the desiccator in order to connect it with an air pump, and so allow drying under a diminished pressure, when the moisture evaporates more rapidly. The fact that, in the usual form of desiccator, the desiccating substance (sulphuric acid) is placed beneath the substance to be dried has the disadvantage that the moist air, being lighter than dry air, distributes itself in the upper portion of the desiccator and not below.

The bell jar, like the receiver of an air pump, should be hermetically closed. In this case desiccation takes place because the sulphuric acid, for instance, first dries the air in the bell jar by absorbing its moisture, the substance to be dried then parting with its moisture to the dry air from which it is again absorbed by the sulphuric acid, &c. Desiccation proceeds still better under the receiver of an air pump, for then the aqueous vapour is formed more quickly than in a bell jar full of air.

From what has been said above, it is evident that the transference of moisture to gases and the absorption of hygroscopic moisture present great resemblance to, but still are not, chemical combinations with water. Water, when combined as hygroscopic water, does not lose its properties and does not form new substances.¹⁵

The attraction of water for substances which dissolve in it is of a different character. In the solution of substances in water a peculiar kind of indefinite combination goes on, a new homogeneous substance being formed from the two substances taken. But here also the bond connecting the substances is very unstable. Water containing different substances in solution boils at a temperature near to its usual boiling-point. From the solution of substances which are lighter than water; as, for example, in the solution of alcohol in water; whilst a heavier substance in dissolving in water gives it a higher specific gravity. Thus salt water is heavier than fresh.¹⁶

Aqueous solutions have a special interest because they are constantly being formed on the earth and in the waters of the earth, in plants and in animals, in chemical processes and in the arts; and these solutions play an important part in the chemical transformations which are everywhere taking place, because a substance in solution presents the most favourable conditions for the execution of chemical changes, which require a mobility of parts and a possible distension of

Hempel, in his desiccator (1891), avoids this by placing the absorbent above the substance to be dried. The process of desiccation can be further accelerated by cooling the upper portion of the desiccator, and so inducing ascending and descending currents of air within the apparatus.

¹⁵ Chappuis, however, determined that in the wetting of 1 gram of charcoal with water, 7 units of heat are evolved, and on pouring carbon bisulphide over 1 gram of charcoal as much as 24 units of heat are evolved. Alumina (1 gram), when moistened with water, evolves $2\frac{1}{2}$ calories. This indicates that in respect to evolution of heat moistening already represents a step towards exothermal combinations (those evolving heat in their formation).

¹⁶ Strong acetic acid ($C_2H_4O_2$), whose specific gravity at 15° is 1.055, does not become lighter on the addition of water (a lighter substance, sp. gr. = 0.999), but heavier, so that a solution of 80 parts of acetic acid and 20 parts of water has a specific gravity of 1.074; and even a solution containing equal parts of acetic acid and water (50 per cent.) has a sp. gr. of 1.065, which is still greater than that of acetic acid itself. This shows the high degree of contraction which takes place on solution. In fact, solutions—and, in general, liquids—on mixing with water, usually decrease in volume.

parts. In dissolving, a solid substance acquires a mobility of parts, and a gas loses its elasticity, and therefore reactions which do not proceed in the undissolved substances often take place in solutions. Further, a substance, distributed in water, evidently breaks up—that is, becomes more like a gas. All these considerations require that, in describing the properties of substances, particular attention should be paid to their relation to water as a universal solvent.

To demonstrate the solubility of gases in water, a gas should be taken which has a high coefficient of solubility—for instance,

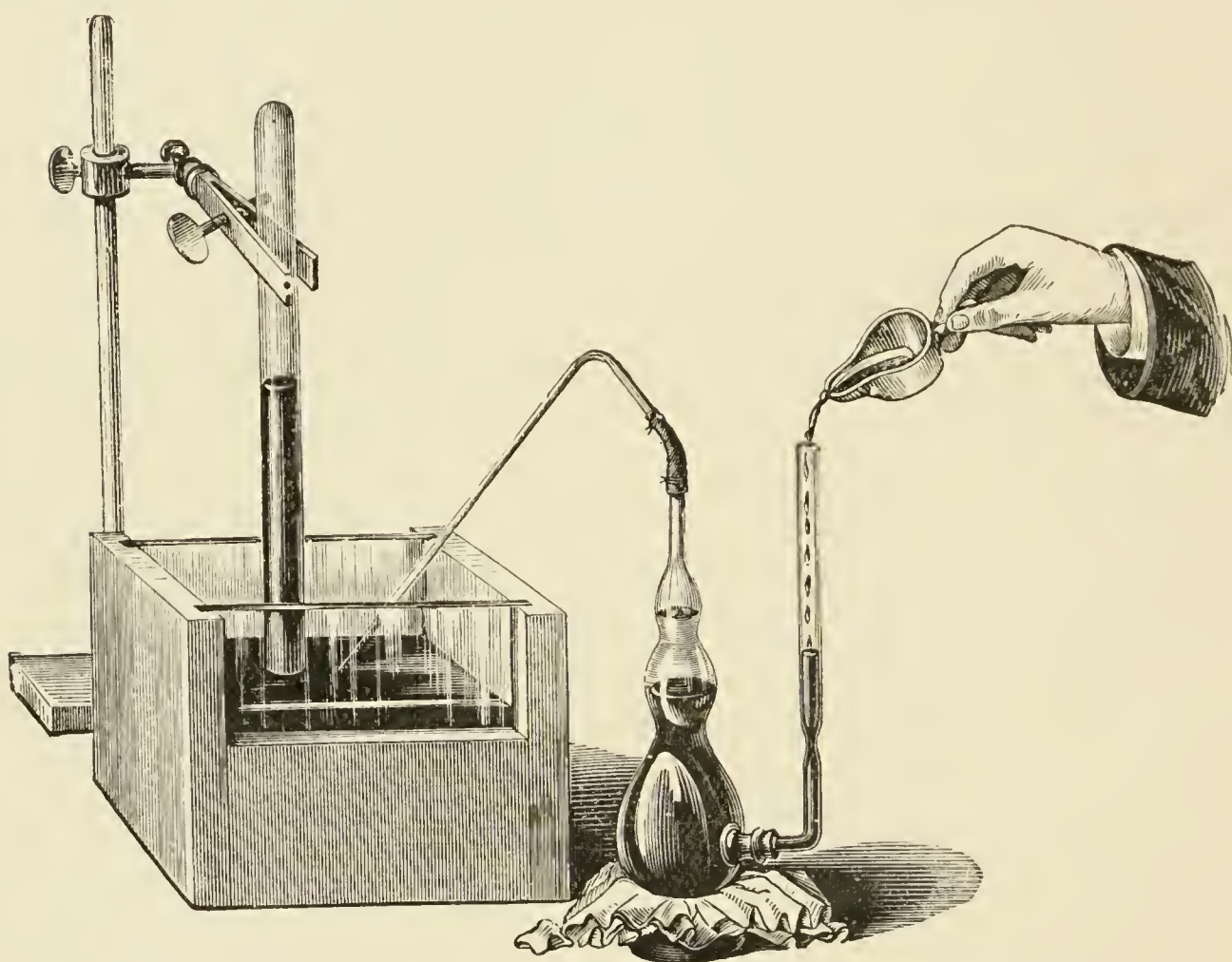


FIG. 14.—Method of transferring a gas into a cylinder filled with mercury, the open end of which is immersed under the mercury in a bath having two glass sides. The apparatus containing the gas is represented on the right. Its upper extremity is furnished with a tube extending under the cylinder. The lower part of the vessel communicates with a vertical tube. If mercury be poured into this tube, the pressure of the gas in the apparatus is increased, and it passes through the gas-conducting tube into the cylinder, where it displaces the mercury, and can be measured or subjected to the action of absorbing agents, such as water.

ammonia. This is introduced into a bell jar (or cylinder, as in fig. 14), which is previously filled with mercury and stands in a mercury bath. If water be then introduced into the cylinder, the mercury will rise, owing to the water dissolving the ammonia gas. If the column of mercury be less than the barometric column, and if there be sufficient water to dissolve the gas, all the ammonia will be absorbed by the water. The water is introduced into the cylinder by a glass pipette with a bent end. The bent end is put into water, and the air is sucked out from the upper end. When full of water, its upper end is

closed with the finger, and the bent end placed in the mercury bath under the orifice of the cylinder. On blowing into the pipette the water will rise, owing to its lightness, to the surface of the mercury in the cylinder. The solubility of a gas like ammonia may be demonstrated by taking a flask full of the gas, and closed by a cork with a tube passing through it. On placing the tube under water, the water will rise into the flask (this may be accelerated by previously warming the flask), and begin to play like a fountain inside it. Both the rising of the mercury and the fountain clearly show the considerable affinity of water for ammonia gas, and the force acting in this dissolution is rendered evident. A certain period of time is required both for the homogeneous intermixture of gases (diffusion) and the process of solution, which depends not only on the extent of the surface of the participating substances, but also on their nature. This may be seen from experiment. Solutions of different substances heavier than water, such as salt or sugar, are poured into tall jars. Pure water is then very carefully poured into these jars (through a funnel) on to the top of the solutions, so as not to disturb the lower stratum, and the jars are then left undisturbed. The line of demarcation between the solution and the pure water will be visible, owing to the difference of their coefficients of refraction. Notwithstanding, however, that the solutions taken are heavier than water, after some time complete intermixture will ensue. Gay-Lussac convinced himself of this fact by this particular experiment, which he conducted in the cellars under the Paris Astronomical Observatory. These cellars are well known as the locality where numerous interesting researches have been conducted, because, owing to their great depth under ground, they have a uniform temperature during the whole year; the temperature does not change during the day, and this was indispensable for the experiments on the diffusion of solutions, in order that no doubt as to the results should arise on account of a daily change of temperature (the experiment lasted several months), which would set up currents in the liquids and intermix their strata. Notwithstanding the uniformity of the temperature, the substance in solution in time ascended into the water and distributed itself uniformly through it, proving that there exists between water and a substance dissolved in it a particular kind of attraction or striving for mutual interpenetration in opposition to the force of gravity. Further, this effort, or rate of diffusion, is different for salt or sugar or other substances.^{16a} It follows therefore that a

^{16a} Graham in the jelly formed by gelatine, and De Vries in gelatinous silica (Chapter XVIII.), most frequently employed coloured (tinted) substances, for instance, $K_2Cr_2O_7$, which showed the rate of diffusion with very great clearness. Prof. Oumoff

peculiar force acts in solution, just as in actual chemical combinations, and solution is determined by a particular kind of motion (by the chemical energy of a substance) which is proper to the substance dissolved and to the solvent.

Graham made a series of experiments similar to those described above, and showed that the **rate of diffusion of solutions**¹⁷ into water is very variable—that is, a uniform distribution of a substance in the water dissolving it is attained in different periods of time with different solutions. Graham compared diffusive capacity with volatility. There are substances which diffuse easily, and there are others which diffuse with difficulty, just as there are more and less volatile substances. Seven hundred cubic centimetres of water were poured into a jar, and by means of a siphon (or a pipette) 100 cubic centimetres of a solution containing 10 grams of a substance were cautiously poured in so as to occupy the lower portion of the jar. After a lapse of several days successive layers of 50 cubic centimetres were taken from the top downwards, and the quantity of substance dissolved in the different layers determined. Thus, common table salt, after fourteen days, gave the following amounts (in milligrams) in the respective layers, beginning from the top: 104, 120, 126, 198, 267, 340, 429, 535, 654, 766, 881, 991, 1,090, 1,187, and 2,266 in the remainder; whilst albumin in the same time gave a very small amount in the first seven layers, and beginning from the eighth layer, 10, 15, 47, 113, 343, 855, 1,892, and in the remainder 6,725 milligrams. Thus, the diffusive power of a solution depends on time and on the nature of the substance dissolved; which fact may serve not only for explaining the process of solution, but also for distinguishing one substance from another. Graham showed that substances which diffuse rapidly through liquids are able to pass rapidly through membranes and to crystallise, whilst substances which diffuse slowly and do not crystallise are **colloids**, that is, resemble glue, and penetrate through a membrane

employed for this purpose glass bulbs of known density which were heavier than water and lighter than the liquid whose diffusion was being studied, and observed the rate of diffusion from the position of the bulbs, which showed the density of the solution and its composition in a given layer.

¹⁷ The researches of Graham, Fick, Nernst, and others showed that the quantity of a dissolved substance which is transmitted (rises) from one stratum of liquid to another in a vertical cylindrical vessel is not only proportional to the time and to the sectional area of the cylinder, but also to the amount of the substance dissolved in a stratum of liquid, so that to every dissolved substance there corresponds its own coefficient of diffusion. The cause of the diffusion of solutions must be considered as essentially the same as that of the diffusion of gases—that is, as dependent on motions peculiar to their molecules—but here most probably those purely chemical, although feebly developed, forces, which incline the substances dissolved to the formation of indefinite compounds with the water, also play their part.

slowly,¹⁸ and form jellies, as will be explained in speaking of silica (Chapter XVIII.)

Hence, if it be desired to increase the rate of solution, recourse must be had to stirring, shaking, or some such mechanical motion.

¹⁸ The rate of diffusion—like the rate of transmission—through membranes, or **dialysis** (which plays an important part in the vital processes of organisms and also in technical processes), presents, according to Graham's researches, a sharply defined change in passing from such crystallisable substances as the majority of salts and acids to substances which are capable of giving jellies (gum, gelatin, &c.) The former diffuse into solutions and pass through membranes much more rapidly than the latter, and Graham therefore distinguishes between **crystalloids**, which diffuse rapidly, and **colloids**, which diffuse slowly. On breaking solid colloids into pieces, a total absence of cleavage is remarked. The fracture of such substances is like that of glue or glass, and is termed 'conchoidal.' Almost all the substances of which animal and vegetable bodies consist are colloids, and this is, at all events partly, the reason why animals and plants have such varied forms, which have no resemblance to the crystalline forms of the majority of mineral substances. The colloid solid substances in organisms—that is, in animals and plants—almost always contain water, and take most peculiar forms, such as networks, granules, hairs, shapeless mucous masses, &c., which are quite different from the forms taken by crystalline substances. When colloids separate out from solutions, or from a molten state, they present a form which is similar to that of the liquid from which they are formed. Glass may be taken as the best example of this. Colloids are distinguishable from crystalloids, not only by the absence of crystalline form, but by many other properties which admit of clearly distinguishing these two classes of solids, as was shown by Graham. Nearly all colloids are capable of passing, under certain circumstances, from a soluble into an insoluble state. The best example is shown by white of eggs (albumin) in the raw and soluble form, and in the hard-boiled and insoluble form. The majority of col-

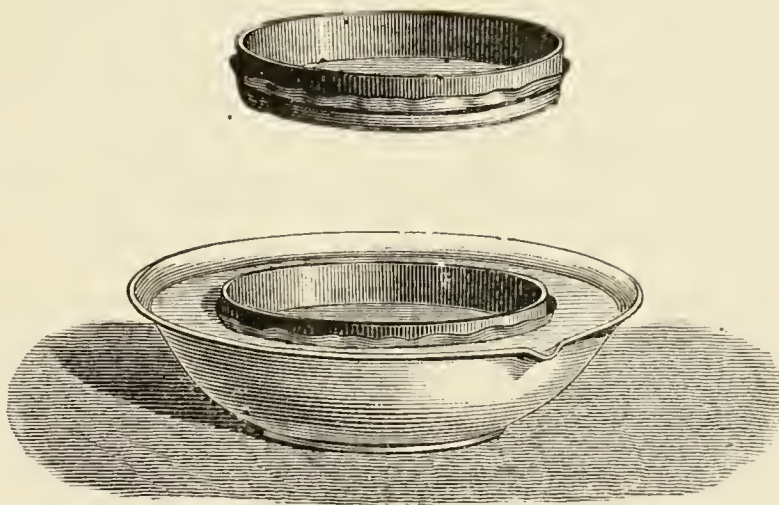


FIG. 15. - Dialyser. Apparatus for the separation of substances which pass through a membrane from those which do not. Description in text.

loids, on passing into an insoluble form in the presence of water, give substances having a gelatinous appearance, which is familiar to everyone in starch, solidified glue, jelly, &c. Thus gelatine or common carpenter's glue, when soaked in water, swells up into an insoluble jelly. If this jelly is heated, it melts, and is then soluble in water, but on cooling it again forms a jelly which is insoluble in water. One of the properties which distinguish colloids from crystalloids is that the former pass very slowly through a membrane, whilst the latter penetrate very rapidly. This may be shown by taking a cylinder, open at both ends, and by covering its lower end with a bladder or with vegetable parchment (unsized paper immersed for two or three minutes in a mixture of sulphuric acid and half its volume of water, and then washed), or any other membranous substance (all such substances are themselves colloids in an insoluble form). The membrane must be firmly tied to the cylinder, so as not to leave any opening. Such an apparatus is called a **dialyser** (fig. 15), and the process of separation of crystalloids from colloids by means of such a membrane is termed **dialysis**. An aqueous solution of a crystalloid or colloid, or a mixture of both, is poured into the dialyser, which is then placed in a vessel containing water, so that the bottom of the membrane is covered with

But if once a uniform solution is formed, it will remain uniform, no matter how heavy the dissolved substance, or how long the solution be left at rest; which fact again shows the presence of a force holding together the particles of the dissolved body and of the solvent.¹⁹

water. Then, after a certain period of time, the crystalloid passes through the membrane, whilst the colloid, if it does pass through at all, does so at an incomparably slower rate. The crystalloid passes through into the water until finally the solution attains the same strength on both sides of the membrane. By replacing the outside water with fresh water, a fresh quantity of the crystalloid may be separated from the dialyser. While the crystalloid is passing through the membrane the colloid remains almost entirely in the dialyser, and therefore mixed solutions of these two kinds of substances may be separated from each other by a dialyser.

¹⁹ The formation of solutions may be considered in two aspects, from a physical and from a chemical point of view; and it is more evident in solutions than in any other department of chemistry how closely these provinces of natural science are allied. On the one hand solutions form a particular case of a physico-mechanical interpenetration of homogeneous substances, and a juxtaposition of the molecules of the substance dissolved and of the solvent, similar to the juxtaposition which is exhibited in homogeneous substances. From this point of view the diffusion of solutions is exactly similar to the diffusion of gases, with only this difference, that the nature and store of energy are different in gases from what they are in liquids, and that in the latter there is considerable friction, whilst in gases there is comparatively little. The penetration of a dissolved substance into water is likened to evaporation, and solution to the formation of vapour. This resemblance was clearly expressed even by Graham, and the Dutch chemist van't Hoff has developed this view of solutions in great detail, having shown (in a memoir in the *Transactions of the Swedish Academy of Science*, 'Lois de l'équilibre chimique dans l'état dilué, gazeux ou dissous,' 1886) that for dilute solutions the *osmotic pressure* follows the same laws (of Boyle, Mariotte, Gay-Lussac, and Avogadro-Gerhardt) as do gases. The **osmotic pressure** of a substance dissolved in water is determined by means of membranes which allow water, but not a substance dissolved in it, to pass through them. This property is found in animal protoplasmic membranes and in porous substances covered with an amorphous precipitate, such as is obtained by the action of copper sulphate on potassium ferrocyanide (Pfeffer, Traube). If a 1 per cent. solution of sugar is placed in such a vessel, which is then closed and placed in water at 70°, the water passes through the walls of the vessel and increases the pressure by 50.5 cm. of the barometric column (= 0.664 atmosphere). If the pressure be artificially increased inside the vessel, then the water will be expelled through the walls. De Vries found a convenient method of determining *isotonic* solutions (those presenting a similar osmotic pressure) by means of the cells of plants. For this purpose a portion of the soft part of the leaves of the *Tradescantia discolor*, for instance, is cut away and moistened with the solution of a given salt and of a given strength. If the osmotic pressure of the solution taken be less than that of the sap contained in the cells, the latter will change their form or shrink; if, on the other hand, the osmotic pressure be greater than that of the sap, then the cells will expand, as can easily be seen under the microscope. By altering the amount of the different salts in solution it is possible to find for each salt the strength of solution at which the cells begin to swell, and at which they will consequently have an equal osmotic pressure. As it increases in proportion to the amount of a substance dissolved per 100 parts of water, it is possible, knowing the osmotic pressure of a given substance—for instance, sugar at various degrees of concentration of solution—and also the composition of isotonic solutions compared with sugar, to determine the osmotic pressure of all the substances investigated. The osmotic pressure of dilute solutions determined in this manner directly or indirectly (from observations made by Pfeffer and De Vries) was shown to follow the same laws as those of the pressure of gases; (1) by doubling or increasing the quantity of a salt (in a given volume) n times, the pressure is

In the consideration of the process of solution, besides the conception of diffusion, another fundamental conception is necessary—namely, that of **saturated solutions**.

doubled or increases n times. Thus, for example, in a solution containing one part of sugar per 100 parts of water, the osmotic pressure (according to Pfeffer) is 53.5 cm. of mercury; if 2 parts of sugar are present, 101.6; if 4 parts, 208.2, and so on; which proves that the ratio is true within the limits of experimental error. (2) Equally concentrated solutions of different substances show very different osmotic pressures, just as equal weights of gases in equal volumes show different pressures. (3) If, for a given dilute solution at 0° , the osmotic pressure equal p_0 , then at t° it will be greater and equal to $p^\circ (1 + 0.00367t)$, i.e., it increases with the temperature in exactly the same manner as the pressure of gases increases. (4) If in dilute solutions of such substances as do not conduct an electric current (for instance, sugar, acetone, and many other organic bodies) the substances be taken in the ratio of their molecular weights (expressed by their formulæ, see Chapter VII.), then not only will the osmotic pressure be the same in all cases, but its magnitude will be determined by that pressure which would be exerted by the vapours of the given substances if they were contained in the space occupied by the solution, just as the pressure of the vapours of molecular quantities of the given substances in equal volumes will be equal, and determined by the laws of Gay-Lussac, Mariotte, and Avogadro-Gerhardt. Those formulæ (Chapter VII., Notes 23 and 24) by which the gaseous state of matter is determined, may also be applied in the present case. Thus, for example, the osmotic pressure p , in centimetres of mercury, of a 1 per cent. solution of sugar, may be calculated according to the formula for gases—

$$Mp = 6200 s (273 + t),$$

where M is the molecular weight, s the weight in grams of a cubic centimetre of vapour, and t its temperature. For sugar $M = 342$ (because its molecular composition is $C_{12}H_{22}O_{11}$). The specific gravity of the solution of sugar is 1.003, so that the weight of sugar s contained in a 1 per cent. solution = 0.01003 gram. The observation was made at $t = 14^\circ$. Hence, according to the formula, we find $p = 52.2$ centimetres. And experiments carried on at 14° gave 53.5 centimetres, which is very near to the above number. (5) For the solutions of salts, acids, and similar substances, which conduct an electric current, the calculated pressure is usually (but not always) a definite or multiple number of times i less than the observed value, and this i for dilute solutions of $MgSO_4$ is nearly 1; for CO_2 , 1; for KCl , $NaCl$, KI , KNO_3 greater than 1 and approximating to 2; for $BaCl_2$, $MgCl_2$, K_2CO_3 , and others between 2 and 3; for HCl , H_2SO_4 , $NaNO_3$, CaN_2O_6 and others nearly 2, and so on. It should be remarked that the above deductions are only applicable (with any degree of accuracy) to dilute solutions. Nevertheless, the arithmetical relation found by van't Hoff between the formation of vapours and the transition into dilute solutions forms an important scientific discovery, which should facilitate the explanation of the nature of solutions, while the osmotic pressure of solutions already forms a very important aspect of their study. In this respect it is necessary to mention that Prof. Konovaloff (1891, and subsequently others also) discovered the dependence (and it may be a sufficient explanation) of the osmotic pressure upon the differences of the pressures of aqueous vapours and aqueous solutions; this, however, takes us into a special province of physical chemistry (certain data are given in Note 49 and following), and to this physical side of the question belongs also one of the extreme consequences of the resemblance of osmotic pressure to gaseous pressure, which is that the concentration of a uniform solution varies in parts which are heated or cooled. Soret (1881) indeed observed that a solution of copper sulphate containing 17 parts of the salt at 20° only contained 14 parts after heating the upper portion of the tube to 80° for a long period of time; that is to say, the lower portion of the solution was richer in salt.

This aspect of solution, which is now being very carefully and fully worked out, may be called the *physical* side. Its other aspect is purely *chemical*, for solution does not take place between any two substances, but requires a special and particular attraction or

Just as moist air may be diluted with any desired quantity of dry air, so also an indefinitely large quantity of a liquid solvent may be taken, and yet a uniform solution will be obtained. But more than a definite quantity of aqueous vapour cannot be introduced into a certain volume of air at any given temperature. The excess above that re-

chemical affinity between them. A vapour or gas permeates any other vapour or gas, but a salt which dissolves in water may not be in the least soluble in alcohol, and is quite insoluble in mercury. In considering solutions as a manifestation of chemical force (and of chemical energy), it must be acknowledged that they are here developed to so feeble an extent that the definite compounds (that is, those formed according to the law of multiple proportions) formed between water and a soluble substance dissociate even at the ordinary temperature, forming a homogeneous system—that is, one in which both the compound and the products into which it decomposes (water and the aqueous compound) occur in a liquid state. The chief difficulty in the comprehension of solutions depends on the fact that the mechanical theory of the structure of liquids has not yet been so fully developed as the theory of gases. The conception of solutions as dissociated definite liquid chemical compounds is based on the following considerations: (1) that there exist certain undoubtedly definite crystallised chemical compounds (such as $\text{H}_2\text{SO}_4, \text{H}_2\text{O}$; or $\text{NaCl}, 2\text{H}_2\text{O}$; or $\text{CaCl}_2, 6\text{H}_2\text{O}$, &c.) which melt on a certain rise of temperature, and then form true solutions; (2) that metallic alloys in a molten condition are real solutions, but on cooling they often give entirely distinct and definite crystallised compounds; (3) that between the solvent and the substance dissolved there are formed, in a number of cases, many undoubtedly definite compounds, such as compounds with water of crystallisation; (4) that the physical properties of solutions, and especially their specific gravities (a property which can be very accurately determined), vary with a change in composition, and in such a manner as would be required by the formation of one or more definite but dissociating compounds. Thus, for example, on adding water to fuming sulphuric acid its density is observed to decrease until it attains the definite composition H_2SO_4 , or $\text{SO}_3 + \text{H}_2\text{O}$, when the specific gravity increases, although on further diluting with water it again falls. Moreover (Mendeléeff, *The Investigation of Aqueous Solutions from their Specific Gravities*, 1887), the increase in specific gravity (ds) varies in all well-known solutions with the proportion of the substance dissolved (dp), and this dependence can be expressed by a formula ($\frac{ds}{dp} = A + Bp$) between the limits of definite compounds whose existence in solutions must be admitted. Thus, for instance, from H_2SO_4 to $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}$ (both of which substances exist as definite compounds in a free state), the fraction $\frac{ds}{dp} = 0.0729 - 0.000749p$ (where p is the percentage amount of H_2SO_4 present). For alcohol, $\text{C}_2\text{H}_6\text{O}$, whose aqueous solutions have been more accurately investigated than all others, the definite compound, $\text{C}_2\text{H}_6\text{O} + 3\text{H}_2\text{O}$, and others must be acknowledged in its solutions.

The two aspects of solution above mentioned and the hypotheses which have up to the present time been applied to the examination of solutions, although they have somewhat different starting-points, will doubtless lead to a general theory of solutions, because the same general laws govern both physical and chemical phenomena, inasmuch as the properties and motions of molecules, which determine physical properties, depend on the motions and properties of atoms, which determine chemical reactions. For details of the questions dealing with theories of solution, recourse must now be had to special memoirs and to works on physical chemistry; for this subject forms one of special interest at the present epoch of the development of our science. In working out chiefly the chemical side of solutions, I consider it to be necessary to reconcile the two aspects of the question: this seems to me to be all the more possible, as the physical side is limited to dilute solutions only, whilst the chemical side deals mainly with strong solutions (see Note 49 and Chap. VII.)

quired for saturation will remain in the liquid state.²⁰ The relation between water and substances dissolved in it is similar. More than a definite quantity of a substance cannot, at a certain temperature, dissolve in a given quantity of water; the excess does not unite with the water. Just as air or a gas becomes saturated with vapour, so water becomes saturated with a substance dissolved in it. If an excess of a substance be added to water which is already saturated with it, it will remain in its original state, and will not diffuse through the water. The quantity of a substance (by volume with gases, or by weight with solids and liquids) which is capable of saturating 100 parts of water is called its **coefficient of solubility** or its **solubility**. In 100 grams of water at 15°, there can be dissolved not more than 35·86 grams of common salt. Consequently its solubility at 15° is equal to 35·86.²¹

²⁰ In the case of limited solution of liquids in liquids, the difference between the solvent and the substance dissolved is clearly seen. The former (that is, the solvent) may be added in an unlimited quantity, and yet the solution obtained will always be uniform, whilst only a definite saturating proportion of the substance dissolved can be taken. Let us take water and ordinary (sulphuric) ether. On shaking the ether with the water, it will be remarked that a portion of it dissolves in the water. If the ether be taken in such a quantity that it saturates the water and a portion of it remains undissolved, then this remaining portion will act as a solvent, and water will become diffused through it and form a saturated solution of water in the ether. Thus two saturated solutions will be obtained. One solution will contain ether dissolved in water, and the other, water dissolved in ether. These two solutions will arrange themselves in two layers, according to their density, the ethereal solution of water being at the top. If the upper ethereal solution be poured off from the aqueous solution, any quantity of ether may be added to it: this shows that the dissolving substance is ether. If water be added to it, it will no longer be dissolved in it, indicating that water saturates the ether; so that here water is the substance dissolved. If we deal in the same way with the lower layer, we shall find that water is the solvent and ether the substance dissolved. By taking different amounts of ether and water, the degree of solubility of ether in water, and that of water in ether, may be easily determined. Water dissolves approximately $\frac{1}{10}$ of its volume of ether, and ether dissolves a very small quantity of water. According to Schuncke (1894) the ethereal solution contains 2·7 per cent. of water at 10°–20°, while the aqueous solution contains 9·6 per cent. of ether at 10°, and 7·5 per cent at 20°. Let us now imagine that the liquid poured in dissolves a considerable amount of water, and that water dissolves a considerable amount of the liquid. Two layers could not be formed, because the saturated solutions would resemble each other, and would therefore intermix in all proportions, as occurs with alcohol and water. This is, consequently, a case of a phenomenon where two liquids present considerable coefficients of solubility in each other, but where it is impossible to say what these coefficients are because it is impossible to obtain a saturated solution.

²¹ The solubility, or coefficient of solubility, of a substance may be determined by various methods. Either a solution is expressly prepared at a given temperature, and using an evident excess of the soluble substance and the quantity of water and of the substance dissolved in it determined by evaporation, desiccation, or other means; or else, as is done with gases, definite quantities of water and of the soluble substance are taken, the amount of the latter remaining undissolved being then determined. So that the solubility is always determined by the presence of an excess of the soluble substance, i.e., it corresponds with a state of equilibrium between the solution, taken in a known quantity (which is one 'phase' or homogeneous substance), and the soluble body (the

It is most important to turn attention to the **existence of the solid insoluble substances of nature**, because on them depends the shape of

other 'phase,' according to the prevalent nomenclature regarding the equilibrium of substances in contact). The theory of solutions and the practical methods of determining the solubility of substances in water and other liquids must be sought for in works on physical chemistry, as this subject now forms a considerable section of itself, and cannot be treated in sufficient detail in the present work, which is chiefly devoted to the study of the chemical elements.

The following description of the mode of determining the solubility of gases must therefore be regarded as an individual example to give the student some idea of the methods practised in the complicated subject of solutions.

The solubility of a gas in water is determined by means of an apparatus called an **absorptiometer** (fig. 16). It consists of an iron stand *f*, on which rests an indiarubber ring. A wide glass tube is placed on this ring, and is pressed down on it by the ring *h* and the screws *i i*. The tube is thus firmly fixed on the stand. A cock *r*, communicating with a funnel *r*, passes into the lower part of the stand. Mercury can be poured into the wide tube through this funnel, which is therefore made of steel, as copper would be affected by the mercury. The upper ring *h* is furnished with a cover *p*, which can be firmly pressed down on to the wide tube, and hermetically closes it by means of an indiarubber ring. The tube *r r* can be raised at will, and so by pouring mercury into the funnel the height of the column of mercury, which produces a pressure inside the apparatus, can be increased. The pressure can also be diminished at will, by letting mercury out

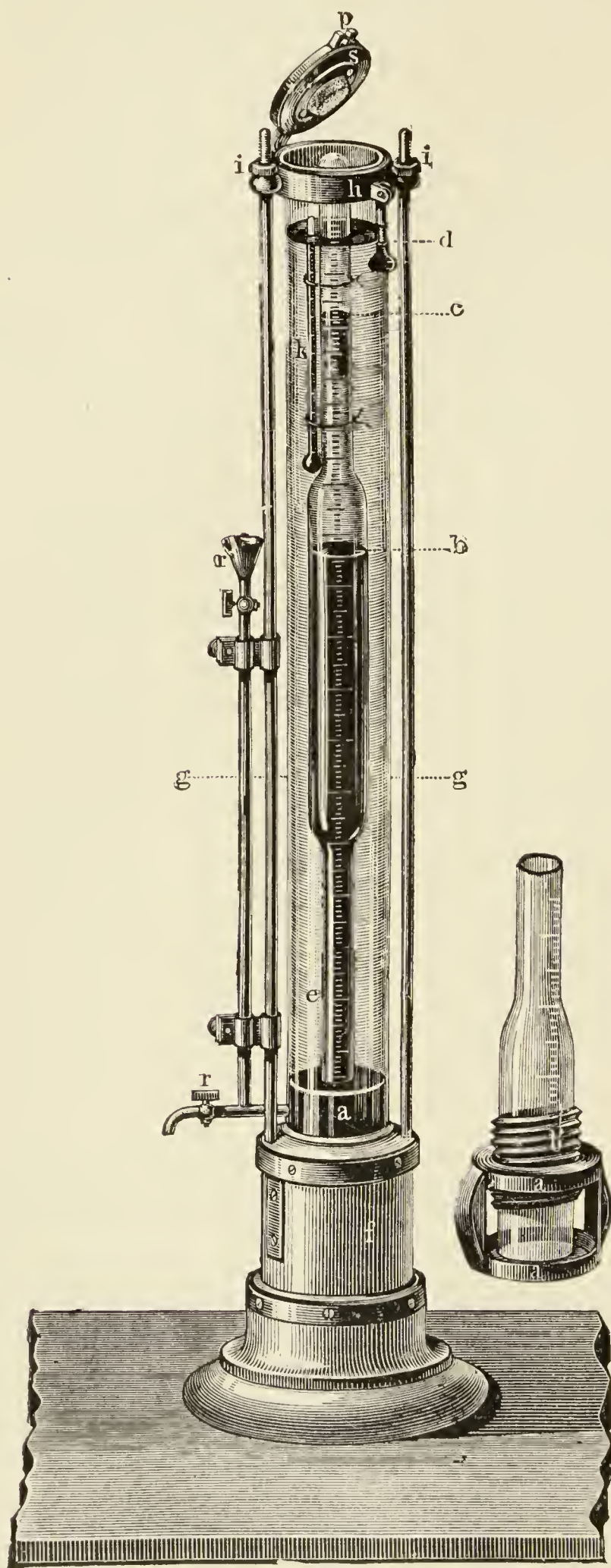


FIG. 16.—Buisen's absorptiometer. Apparatus for determining the solubility of gases in liquids.

the substances of the earth's surface, and of plants and animals. There is so much water on the earth's surface that were the surface of

through the cock *r*. A graduated tube *e*, containing mercury and also the gas and liquid to be experimented on, is placed inside the wide tube. This tube is graduated in millimetres for determining the pressure, and it is calibrated in volumes, so that the number of volumes occupied by the gas and liquid dissolving it can be readily calculated. This tube can also be easily removed from the apparatus. The lower portion of this tube when removed from the apparatus is shown to the right of the figure. It will be observed that its lower end is furnished with a male screw *b*, fitting into a nut *a*. The lower surface of the nut *a* is covered with indiarubber, so that on screwing up the tube its lower end presses upon the indiarubber, and thus hermetically closes the whole tube, for its upper end is fused up. The nut *a* is furnished with arms *c c*, and in the stand *f* there are corresponding spaces, so that when the screwed-up internal tube is fixed into the stand *f*, the arms *c c* fix into these spaces, thus enabling the internal tube to be fixed on to the stand *f*. When the internal tube is fixed in the stand, the wide tube is placed in position, and mercury and water are poured into the space between the two tubes, communication being then opened between the inside of the tube *e* and the mercury between the interior and exterior tubes. This is done by either revolving the inner tube *e*, or by a key turning the nut about the bottom part of *f*. The tube *e* is filled with gas and water as follows: the tube is removed from the apparatus, filled with mercury, and the gas to be experimented on is passed into it (over a pneumatic trough). The volume of the gas is measured, the temperature and pressure determined, and the volume it would occupy at 0° and 760 mm. calculated. A known volume of water is then introduced into the tube. The water must be previously boiled, so as to be quite freed from air in solution. The tube is then closed by screwing it down on to the india-rubber on the nut. It is then fixed on to the stand *f*, mercury and water are poured into the intervening space between it and the exterior tube, which is then screwed up and closed by the cover *p*, and the whole apparatus left at rest for some time, so that the tube *e* and the gas in it may attain the same temperature as that of the surrounding water, which is marked by a thermometer *k* tied to the tube *e*. The inner tube is then again closed by turning it in the nut, the cover *p* again shut, and the whole apparatus shaken in order that the gas in the tube *e* may completely saturate the water. After several shakings, the tube *e* is again opened by turning it in the nut, and the apparatus left at rest for a certain time; it is then closed and again shaken, this being repeated until the volume of the gas does not diminish after a fresh shaking—that is, until saturation ensues. Observations are then made of the temperature, the height of the mercury in the inner tube, and the level of the water in it, and also of the level of the mercury and water in the outer tube. All these data are necessary in order to calculate the pressure under which the solution of the gas takes place, and what volume of gas remains undissolved, and also the quantity of water which serves as the solvent. By varying the temperature of the surrounding water, the amounts of gas dissolved at different temperatures may be determined. By means of this apparatus Bunsen, Carius, and many others determined the solubilities of various gases in water, alcohol, and certain other liquids. If in a determination of this kind it is found that *n* cubic centimetres of water at a pressure *h* dissolve *m* cubic centimetres of a given gas, measured at 0° and 760 mm., when the temperature at which solution took place was *t*°, then it follows that at the temperature *t* **the coefficient of solubility of the gas** in 1 volume of the liquid will be equal to $\frac{m}{n} \times \frac{760}{h}$.

This formula is very clearly understood from the fact that the coefficient of solubility of a gas is that quantity (by volume or weight) measured at 0° and 760 mm., which is absorbed at a pressure of 760 mm. by 1 part or 100 parts of a liquid. If *n* cubic centimetres of water absorb *m* cubic centimetres of a gas, then one cubic centimetre absorbs $\frac{m}{n}$.

If $\frac{m}{n}$ c.c. of a gas are absorbed under a pressure of *h* mm., then, according to the law of

substances formed of soluble matters it would constantly change, and, however substantial their forms might be, mountains, river banks and sea shores, plants and animals, or the habitations and coverings of men, could not exist for any length of time.²²

Substances which are easily soluble in water bear a certain resemblance to it. Thus sugar and salt in many of their superficial features remind one of ice. Metals, which are not soluble in water, have no points in common with it, whilst on the other hand they dissolve each other in a molten state, forming alloys, just as oily substances dissolve each other; for example, tallow is soluble in petroleum and in olive oil, although they are all insoluble in water. From this it is evident that the **analogy between the substances forming a solution** is of some the variation of solubility of a gas with the pressure, there would be dissolved, under a pressure of 760 mm., a quantity standing in the same ratio to $\frac{m}{n}$ as 760 : h . In determining the residual volume or weight of gas, its moisture (note 1) must be taken into consideration. L. Winkler (1888–1902) of Buda-Pesth determined the solubility of gases by a more perfect method.

The solubility (expressed in volumes) of many gases in water is given in note 30. Below are given the numbers of grams of several substances saturating 100 grams of water—that is, their coefficients of solubility by weight at three different temperatures under a pressure of 760 mm.

—		At 0°	At 20°	At 100°
Gases	Oxygen, O ₂	$\frac{6}{1000}$	$\frac{4}{1000}$	—
	Carbonic anhydride, CO ₂	$\frac{35}{100}$	$\frac{18}{100}$	—
	Ammonia, NH ₃	90.0	51.8	7.3
Liquids	Phenol, C ₆ H ₆ O	4.9	5.2	∞
	Amyl alcohol, C ₅ H ₁₂ O	4.4	2.9	—
	Sulphuric acid, H ₂ SO ₄	∞	∞	∞
Solids	Gypsum, CaSO ₄ · 2H ₂ O	$\frac{1}{2}$	$\frac{1}{4}$	$\frac{1}{5}$
	Alum, AlKSO ₄ · 12H ₂ O	3.3	15.4	357.5
	Anhydrous sodium sulphate, Na ₂ SO ₄	4.5	20	43
	Common salt, NaCl	35.7	36.0	39.7
	Nitre, KNO ₃	13.3	31.7	246.0

Sometimes a substance is so slightly soluble that it may be considered as insoluble. Many such substances are met with both in solids and liquids, and such a gas as oxygen, although it does dissolve, does so in so small a proportion by weight that it might be considered as zero did not the solubility of even so little oxygen play an important part in nature (as in the respiration of fishes), and were not an infinitesimal quantity of a gas by weight so easily measured by volume. The sign ∞, which stands on a line with sulphuric acid in the above table, indicates that it intermixes with water in all proportions. This is the case with many liquids.

²² Just as the existence must be admitted of substances which are completely undecomposable (chemically) at the ordinary temperature—and of substances which are entirely non-volatile at such a temperature (as wood and gold), although capable of decomposing (wood) or volatilising (gold) at a higher temperature—so also the existence must be admitted of substances which are totally insoluble in water. It must be remarked, besides, that water in a number of cases does not dissolve a substance as such, but acts on it chemically and forms a soluble substance. Thus glass and many rocks, especially if taken as powder, are chemically changed by water, but are not directly soluble in it.

importance, and as aqueous and all other solutions are liquids, there is good reason to believe that in the process of solution solid and gaseous substances change physically and pass into a liquid state. These considerations elucidate many points of solution—as, for instance, the variation of the coefficient of solubility with the temperature and the evolution or absorption of heat in the formation of solutions.

The solubility—that is, the quantity of a substance necessary for saturation—**varies with the temperature**, and, further, with a rise in temperature the solubility of solid substances generally increases, whilst that of gases decreases: this might be expected, as solid substances by heating, and gases by cooling, approach to a liquid or dissolved state.²³ A graphic method is often employed to express the variation of solubility with temperature. On the axis of abscissæ or on a horizontal line, temperatures are marked out and perpendiculars are raised corresponding with each temperature and having lengths determined by the solubilities of the salt at the various temperatures—expressing, for instance, one part by weight of a salt in 100 parts of water by one unit of length, such as a millimetre. By joining the summits of the perpendiculars, a curve is obtained which expresses the degree of solubility at different temperatures. For solids, the curve is generally an ascending one—i.e., it recedes from the horizontal line as the temperature rises. These curves clearly show by their inclination the degree of rapidity of increase in solubility with the temperature. Having determined several points of a curve—that is, having made determinations of the solubilities for several temperatures—the solubilities at intermediate temperatures may be determined from the form of the curve so obtained: in this way the empirical law of solubility may be examined.^{23a}

²³ Beilby (1883) experimented on paraffin, and found that one litre of solid paraffin at 21° weighed 874 grams, and in the liquid state at its melting-point, 38°, 783 grams; at 49°, 775 grams, and at 60°, 767 grams; hence the weight of a litre of liquefied paraffin would be 795.4 grams at 21°, supposing that it could remain liquid at that temperature. By dissolving solid paraffin in lubricating oil at 21°, Beilby found that 795.6 grams occupy one cubic decimetre, from which he concluded that the solution contained liquefied paraffin.

^{23a} Gay-Lussac was the first to have recourse to such a graphic method of expressing solubility, and he considered, in accordance with the general opinion, that by joining up the summits of the ordinates in one harmonious curve it is possible to express the entire change of solubility with the temperature. Now, there are many reasons for doubting the accuracy of such an admission, for there are undoubtedly critical points in curves of solubility (for example, of sodium sulphate, as shown further on), and it may be that definite compounds of dissolved substances with water, in decomposing within known limits of temperature, give critical points more often than would be imagined; it may even be, indeed, that, instead of a continuous curve, solubility should be expressed—if not always, then not infrequently—by straight or broken lines. The modern theory of phases (which is treated more fully in *Physical Chemistry*; see also Chap. XXIV., note 9a) fully explains such breaks in the curve of solubility, which occur when the soluble substance and water are able to form crystals of various compositions (different crystallohydrates) and crystalline forms (see note 24). According to Ditte, the solubility of

The results of research have shown that the solubility of certain salts—as, for example, common table salt—varies comparatively little with the temperature, whilst for other substances the solubility increases by equal amounts for equal increments of temperature. Thus, for example, for the saturation of 100 parts of water by potassium chloride there is required 29·2 parts of the salt at 0°, 34·7 at 20°, 40·2 at 40°, 45·7 at 60°, and so on, the solubility increasing by 2·75 parts by weight of the salt for every 10°. Therefore the solubility of the potassium chloride in water may be expressed by a simple equation: $a = 29·2 + 0·275t$, where a represents the solubility at t° . For other salts more complicated equations are required. For example, for nitre: $a = 13·3 + 0·574t + 0·01717t^2 + 0·0000036t^3$, which shows that when $t = 0^\circ$, $a = 13·3$; when $t = 10^\circ$, $a = 20·8$, and when $t = 100^\circ$, $a = 246·0$.

The variation in the solubility of salts, &c., with a rise or fall of temperature is often taken advantage of, especially in technical work, for the separation of salts mixed with each other. Thus a mixture of potassium and sodium chlorides (a mixture met with in nature at Stassfurt) is separated by subjecting a saturated solution alternately to boiling (evaporation) and cooling. The sodium chloride separates out in proportion to the amount of water expelled from the solution by sodium nitrate, NaNO_3 , per 100 parts of water is expressed by the following figures:—

0°	4°	10°	15°	21°	29°	36°	51°	68°
66·7	71·0	76·3	80·6	85·7	92·9	99·4	113·6	125·1

In my opinion (1881) these data should be expressed with exactitude by a straight line, $67·5 + 0·87t$. The experiments made by Ditte showed that all saturated solutions between 0° and $-15·7^\circ$ have such a composition, and that at the latter temperature the solution completely solidifies into one homogeneous whole whose composition is approximately $\text{NaNO}_3, 7\text{H}_2\text{O}$. Thus the solubility of sodium nitrate is expressed by a broken straight line. Étard (1888) discovered a similar phenomenon in many of the sulphates. Brandes, in 1830, showed a diminution in solubility below 100° for manganese sulphate. The percentage by weight (i.e., per 100 parts of the solution, and not of water) of saturated ferrous sulphate (FeSO_4) solution from -2° to $+65^\circ$ is given by $13·5 + 0·3784t$ —that is, the solubility of the salt increases. From 65° to 98° the solubility remains constant, and from 98° to 150° it falls and is expressed by $104·35 - 0·6685t$. Hence, at about $+156^\circ$ the solubility should become zero; and this has been confirmed by experiment. I find that Étard's formula gives 38·1 per cent. of salt at 65° and 38·8 per cent. at 92°, and this maximum amount of salt in solution corresponds very nearly with the composition $\text{FeSO}_4, 14\text{H}_2\text{O}$, which requires 37·6 per cent. From what has been said, it is evident that the data concerning solubility require a new method of investigation, which should take into account the entire scale of solubility—from the formation of completely solidified solutions (cryohydrates, which we shall speak of presently) to either the separation of salts from their solutions, should this take place at a higher temperature (for manganese and cadmium sulphates there is complete separation, according to Étard), or the attainment of a constant solubility (for potassium sulphate the solubility, according to Étard, remains constant from 163° to 220° and equals 24·9 per cent.). The following are Étard's data for several salts (parts of salt per 100 parts of solution). KNO_3 : up to 70°, $24·0 + 0·7100t$; from 70° to 125°, $59·5 + 0·3727t$; from 125° to 338°, $80·0 + 0·0938t$. For NaNO_3 : from 5° to 64°, $39·0 + 0·2825t$; from 64° to 313°, $58·5 + 0·1666t$. For NaCl : from 0° to 250°, $25·8 + 0·0248t$ (see Chap. XII., note 4, &c.)

boiling, and is removed, whilst the potassium chloride separates out on cooling, as the solubility of this salt decreases rapidly as the temperature falls. Nitre, sugar, and many other soluble substances are purified (refined) in a similar manner.

Although in the majority of cases the solubility of solids increases with rise of temperature, yet there are some solid substances whose solubilities decrease on heating. A particularly instructive example is found in the case of Glauber's salt, or sodium sulphate. If this salt be taken after ignition (deprived of its water of crystallisation), its solubility in 100 parts of water varies with the temperature in the following manner: at 0° , 5 parts of the salt form a saturated solution; at 20° , 20 parts of the salt, while at 33° more than 50 parts are required. The solubility, as will be seen, increases with the temperature, but above 33° it suddenly diminishes, and at a temperature of 40° less than 50 parts, at 60° only 45 parts, and at 100° about 43 parts, dissolve in 100 parts of water. This phenomenon may be traced to the following facts: First, this salt forms various compounds with water, as will be afterwards explained; secondly, at 33° the compound $\text{Na}_2\text{SO}_4 + 10\text{H}_2\text{O}$, formed from the solution at lower temperatures, melts; and thirdly, on evaporation at a temperature above 33° an anhydrous salt, Na_2SO_4 , separates out, while at lower temperatures the anhydrous salt converts the water into a solid state without itself passing into solution (see Chap. XII., note 8). It will be seen from this example how complicated such an apparently simple phenomenon as solution really is; and all data concerning solutions lead to the same conclusion.²⁴ This complexity becomes evident also

²⁴ First of all we must remember that saturation of a solution can only refer to the substance which is present in the solution, and not to that which was originally taken for making the solution. Thus, for instance, if a given salt occurs in two crystalline forms A and B (that is, it is dimorphous), stable within certain limits of temperature, these will possess different solubilities. Suppose A to be more soluble than B. A saturated solution of B will be able to dissolve a further amount of A until saturation be reached. If we now pour off this solution from the excess of A, and add a further quantity of B, then a portion of the salt will separate out from the solution in the form B, although the same solution, if evaporated in the presence of an excess of A, would deposit the variety A; and since many anhydrous salts deposit solid, frequently dimorphous, compounds with water from their solutions, it is evident that the different phenomena concerned in saturation may be most complex (see, for instance, Chap. XIV., note 50, for CaCl_2 ; Chap. XXII., note 23, for Fe_2Cl_6). As an instance of this, we may take the solubility of sodium carbonate calculated as parts of anhydrous salt per 100 parts of water:

Solid phase	At 0°	At 20°
$\text{Na}_2\text{CO}_3, 10\text{H}_2\text{O}$	7	22
$\text{Na}_2\text{CO}_3, 7\text{H}_2\text{O}$ – cubic	20	39
$\text{Na}_2\text{CO}_3, 7\text{H}_2\text{O}$ – rhombic	31	46

The solubility of the anhydrous salt, Na_2CO_3 , cannot be given, because at these

on investigating the **heat of solution**. If solution consisted of a physical change only, then in the solution of gases there would be evolved—and in the solution of solids there would be absorbed—just that amount of heat corresponding with the change of state; but in reality a larger amount of heat is always evolved in the solution of gases, and less is absorbed in the solution of solids than is required by theory, owing to the fact that in the process of solution chemical combination takes place, accompanied by an evolution of heat. Seventeen grams of ammonia (this weight corresponds with its formula NH_3), in passing from a gaseous to a liquid state, evolve 4,400 units of heat (latent heat), that is, the quantity of heat necessary to raise the temperature of 4,400 grams of water 1° . The same quantity of ammonia, in dissolving in an excess of water, evolves twice as much heat—namely, 8,800 units—showing that the combination with water is accompanied by the evolution of 4,400 units of heat. Further, the chief part of this heat is generated when the gas dissolves in small quantities of water, so that 17 grams of ammonia, in dissolving in 18 grams of water (this weight corresponds with its composition H_2O), evolve 7,535 units of heat, and therefore the formation of the solution $\text{NH}_3 + \text{H}_2\text{O}$ evolves 3,135 units of heat beyond that due to the change of state. Since in the solution of gases the heats of liquefaction (of physical change of state) and of chemical combination with water are both positive (+), it follows that in the *solution of gases* in water *heat is always evolved*. This phenomenon is different in the solution of solid substances, because the passage from a solid to a liquid state is accompanied by an absorption of heat (—heat), whilst their chemical combination with water is accompanied by an evolution of heat (+heat); consequently their sum may either be a cooling effect, when the positive (chemical) portion of the heat is less than the negative (physical), or it may be, on the contrary, a heating effect. This is actually found to be the case. 124 grams of sodium thiosulphate (employed in photography), $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, in melting (at 48°) absorb 9,700 units of heat, but in dissolving in a large quantity of water at the ordinary temperature they absorb 5,700 units of heat, which shows that, notwithstanding the cooling effect observed in the process of solution, an evolution of heat (about +4,000 units) takes place in the act of the chemical combination of the salt with water.²⁵ But in most cases

temperatures it forms a solid crystallhydrate, and *if brought into solution in excess, it precipitates a portion of the salt from the solution* in the form of the solid phase of the crystallhydrate (compare Chap. XII., note 8).

²⁵ The latent heat of fusion is determined at the temperature of fusion, whilst solution takes place at the ordinary temperature; and one must think that at this temperature the latent heat would be different, just as the latent heat of evaporation varies with

solid substances in dissolving in water evolve heat, notwithstanding the passage into a liquid state, indicating so considerable an evolution of (+) heat in the act of combination with water as to exceed the absorption of (−) heat dependent on the passage into a liquid. Thus, for instance, calcium chloride, CaCl_2 , magnesium sulphate, MgSO_4 , and many other salts evolve heat in dissolving; for example, 60 grams of magnesium sulphate evolve about 10,000 units of heat. Therefore, *in the solution of solids or liquids in water either a cooling*²⁶ *or a* the temperature (see note 11). Besides which, in the process of solution, disintegration of the particles of both the solvent and the substance dissolved takes place; a change which in its mechanical aspect resembles evaporation, and must therefore consume much heat. The heat emitted in the solution of a solid must therefore be considered (Personne) as composed of three factors: (1) positive, the effect of combination; (2) negative, the effect of transference into a liquid state; and (3) negative, the effect of disintegration. In the solution of a liquid by a liquid the second factor is removed; and therefore if the heat evolved in combination is greater than that absorbed in disintegration a heating effect is observed, and in the reverse case a cooling effect; and, indeed, sulphuric acid, alcohol, and many other liquids evolve heat in dissolving in each other. But the solution of chloroform in carbon bisulphide (Bussy and Binget), or of phenol (or aniline) in water (Alexéeff) produces cold. In the solution of a small quantity of water in acetic acid (Abasheff), or hydrocyanic acid (Bussy and Binget), or amyl alcohol (Alexéeff), cold is produced, whilst when these substances are dissolved in an excess of water heat is evolved.

The relation existing between the solubility of solid bodies and the heat and temperature of fusion and solution has been studied by many investigators, and more especially (1893) by Schröder, who states that in the solution of a solid body in a solvent which does not act chemically upon it a very simple process takes place, which differs but little from the intermixture of two gases which do not react chemically upon each other. To such a case the following relation between the heat of solution Q and the heat of fusion p is applicable: $\frac{p}{T_0} = \frac{Q}{T} = \text{constant}$, where T_0 and T are the absolute (from -273°)

temperatures of fusion and saturation. In the case of naphthalene, for instance, the calculated and observed magnitudes of the heat of solution differ but slightly from each other.

The fullest information concerning the solution of liquids in liquids has been obtained by W. T. Alexéeff (1883–1885); but these data are, however, far from being sufficient to solve the mass of problems respecting this subject. He showed that the solubility of phenol, $\text{C}_6\text{H}_5\text{O}$, in water, and the converse, is limited up to 70° , whilst above this temperature the two intermix in all proportions. This is seen from the following figures, where p is the percentage amount of phenol and t the temperature at which the solution becomes turbid—that is, that at which it is saturated:—

$p=7.12$	10.20	15.31	26.15	28.55	36.70	48.86	61.15	71.97
$t=1^\circ$	45°	60°	67°	67°	67°	65°	53°	20°

It is exactly the same with the solutions of benzene, aniline, and other substances in molten sulphur. Alexéeff discovered a similar complete intermixture for secondary butyl alcohol and water at about 107° ; at lower temperatures the solubility is not only limited, but between 50° and 70° it is at its minimum, both for solutions of the alcohol in water and for water in the alcohol; and at a temperature of 5° both solutions exhibit a fresh change in their scale of solubility, so that a solution of the alcohol in water, which is saturated between 5° and 40° , will become turbid when heated to 60° . In the solution of liquids in liquids Alexéeff observed a lowering in temperature (an absorption of heat) and an absence of change in specific heat (contrary to the calculated results for the mixture) much more frequently than had been done by previous observers.

²⁶ The cooling effect produced in the solution of solids (and also in the expansion of gases and in evaporation) is applied to the **production of low temperatures**. Ammonium

*heating*²⁷ effect is produced, according to the difference of the reacting affinities. When they are considerable—that is, when water is with difficulty separated from the resultant solution, and only with a rise of temperature—then much heat is evolved in the process of solution, just as in many reactions of direct combination, and therefore a considerable heating of the solution is observed. Of such a kind, for instance, are the solutions of sulphuric acid (oil of vitriol, H_2SO_4), and of caustic soda (NaHO), &c., in water.²⁸

nitrate is very often used for this purpose; in dissolving in water it absorbs 77 units of heat for each part by weight. On evaporating the solution thus formed, the solid salt is re-obtained. The application of the different **freezing mixtures** is based on the same principle. Snow or broken ice frequently enters into the composition of these mixtures, advantage being taken of its latent heat of fusion in order to obtain the lowest possible temperature (without altering the pressure or employing heat, as in other methods of obtaining a low temperature). For laboratory work recourse is most often had to a mixture of three parts of snow and one part of common salt, which causes the temperature to fall from 0° to -21° C. Potassium thiocyanate, KCNS , mixed with water ($\frac{3}{4}$ by weight of the salt) gives a still lower temperature. By mixing ten parts of crystallised calcium chloride, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, with seven parts of snow, the temperature may even fall from 0° to -55° .

²⁷ The heat which is evolved in solution, or even in the dilution of solutions, is also sometimes made use of in practice. Thus caustic soda (NaHO), in dissolving or on the addition of water to a strong solution of it, evolves so much heat that it can replace fuel. In a steam boiler, which has been previously heated to the boiling-point, another boiler is placed containing caustic soda, and the exhaust steam is made to pass through the latter; the formation of steam then goes on for a fairly long time without any further heating. Norton makes use of this for smokeless street locomotives.

²⁸ The temperatures obtained by mixing monohydrated sulphuric acid, H_2SO_4 , with

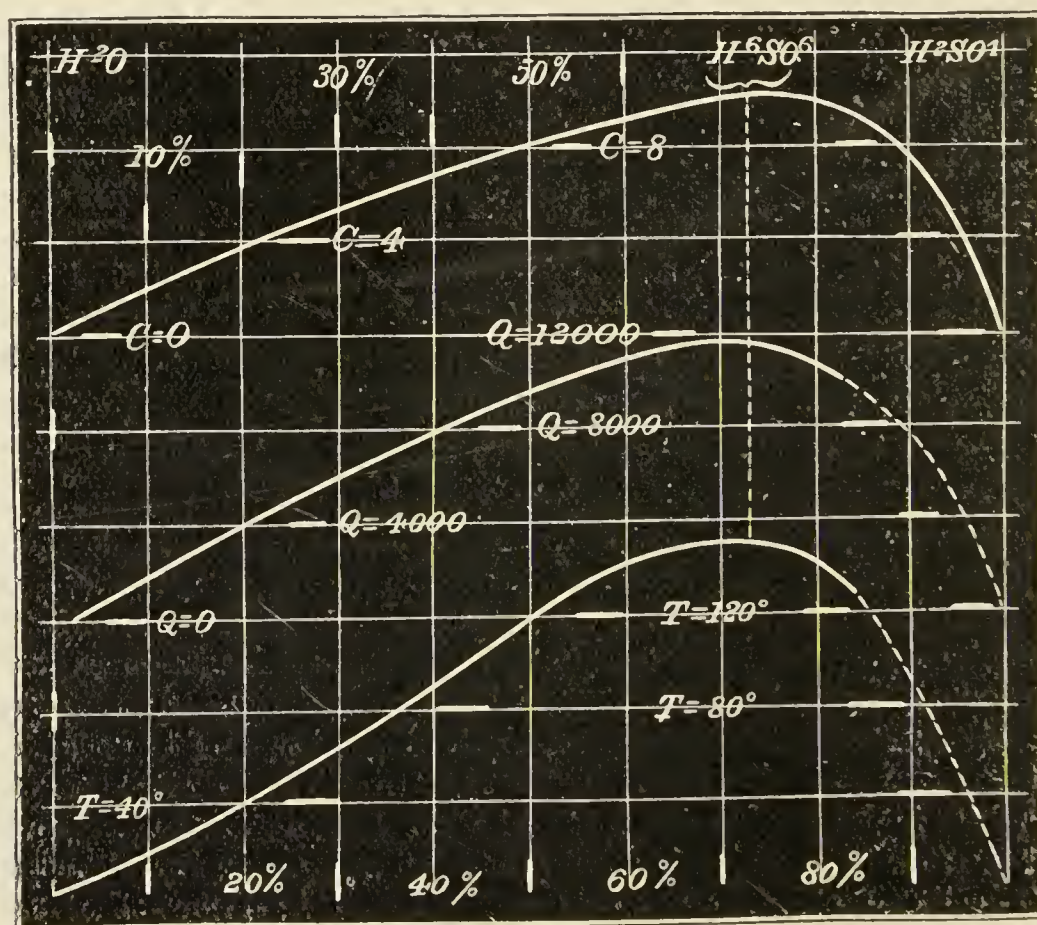


FIG. 17.—Curves expressing the contraction, quantity of heat, and rise of temperature produced by mixing sulphuric acid with water. Percentage of H_2SO_4 is given along the axis of abscissæ.

Solution is a reversible reaction ; for, if the water be expelled from a solution, the substance originally taken is obtained again. But it must be borne in mind that the expulsion of the water taken for solution is not always accomplished with equal facility, because water has different degrees of chemical affinity for the substance dissolved. Thus, if a solution of sulphuric acid, which mixes with water in all proportions, be heated, it will be found that very varying temperatures are required to expel the water. When in a large excess, water is given off at a temperature slightly above 100° ; but if it be in only a small proportion, there is such an affinity between it and the sulphuric acid that at 120° , 150° , 200° , and even at 300° , water is still retained by the sulphuric acid. The bond between the remaining quantity of water and the sulphuric acid is evidently stronger than that between the sulphuric acid and the excess of water. The force acting in solutions is consequently of different intensity, starting from so feeble an attraction that the properties of water—as, for instance, its power of evaporation—are but very little changed, and ending with strong attraction between the water and the substance dissolved in or chemically combined with it.

The solubility of gases, which is usually measured by the volume of gas ²⁹ (at 0° and 760 mm. pressure) per 100 volumes of water, varies

different quantities of water are shown on the lowest curve in fig. 17, the relative proportions of the two substances being expressed in percentages by weight along the horizontal axis. The greatest rise of temperature is 149° . It corresponds with the greatest evolution of heat (given on the middle curve) for a definite volume (100 c.c.) of the solution produced. The top curve expresses the degree of contraction corresponding with 100 volumes of the solution produced. The greatest contraction, as also the greatest rise of temperature, corresponds with the formation of a trihydrate, $\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ (containing 73.1 per cent. H_2SO_4). Similar relations probably hold for other solutions, although all the phenomena (contraction, evolution of heat, and rise of temperature) are very complex, and are dependent on many circumstances. One would think, however, judging from the above examples, that all other influences are feebler in their action than chemical attraction, especially when this is so considerable as it is between sulphuric acid and water.

²⁹ If a volume of gas v be measured under a pressure of h mm. of mercury (at 0°) and at a temperature t° Centigrade, then, according to the combined laws of Boyle, Mariotte, and Gay-Lussac, its volume at 0° and 760 mm. will equal the product of v into h divided by the product of 760 into $1 + at$, where a is the coefficient of expansion of gases, which is equal to 0.00360. The weight of the gas will be equal to its volume at 0° and 760 mm., multiplied by its density referred to air and by the weight of one volume of air at 0° and 760 mm., the weight of a litre of air under these conditions being 1.293 gram. If the density of the gas be given in relation to hydrogen, this must be divided by 14.4 to make it refer to air. If the gas be measured when saturated with aqueous vapour, then it must be reduced to the volume and weight of the gas when dry, according to the rules given in note 1. If the pressure be determined by a column of mercury having a temperature t° , then by dividing the height of the column by $1 + 0.00018t$ the corresponding height at 0° is obtained. If the gas be enclosed in a tube in which a liquid stands above the level of the mercury, the height of the column of the

not only with the nature of the gas (and also of the solvent), and with the temperature, but also with the pressure, because gases themselves change their volume considerably with change of pressure. As might be expected, (1) gases which are easily liquefied (by pressure and cold) are more soluble than those which are liquefied only with difficulty. Thus, in 100 volumes of water only two volumes of hydrogen or nitrogen dissolve at 0° and 760 mm., three volumes of carbonic oxide, four volumes of oxygen, &c., for these are gases which are liquefied with difficulty; whilst there dissolve 180 volumes of carbonic anhydride, 130 of nitrous oxide, and 437 of sulphurous anhydride, for these are gases which are fairly easily liquefied. (2) The solubility of a gas is diminished by heating, this being easily intelligible from what has been said previously—the elasticity of a gas becomes greater, that is, it is removed further from a liquid state. Thus 100 volumes of water at 0° dissolve 2·5 volumes of air, but at 20° only 1·7 volume. For this reason cold water, when brought into a warm room, parts with a portion of the gas dissolved in it.³⁰ (3) The quantity of the gas liquid being H and its density D, then the gas will be under a pressure equal to the barometric pressure less $\frac{HD}{13\cdot59}$, 13·59 being the density of mercury. By these methods

the **quantity of a gas** is determined, and its observed volume reduced to normal conditions or to parts by weight. The physical data concerning vapours and gases must be continually kept in sight in dealing with and measuring gases. The student must become perfectly familiar with the calculations relating to gases.

³⁰ According to Bunsen, Winkler, Timoféeff, and others, 100 vols. of water under a pressure of one atmosphere absorb the following volumes of gas (measured at 0° and 760 mm.) :—

	1	2	3	4	5	6	7	8	9	10	11
0°	4·82	2·35	2·15	179·7	3·54	130·5	437·1	688·6	5·4	104960	7·38
20°	3·10	1·54	1·83	90·1	2·32	67·0	290·5	362·2	3·5	65400	4·71

1, oxygen; 2, nitrogen; 3, hydrogen; 4, carbonic anhydride; 5, carbonic oxide; 6, nitrous oxide; 7, hydrogen sulphide; 8, sulphurous anhydride; 9, marsh gas; 10, ammonia; 11, nitric oxide. The decrease of solubility with rise of temperature varies for different gases and increases with the molecular weight of the gas. It is shown by calculation that this decrease varies (Winkler at Buda-Pesth) as the cube root of the molecular weight of the gas. This is seen from the following table:

Decrease of solubility per 20° in per cent.		Cube root of molecular weight	Ratio between decrease and cube root of mol. wt.
H ₂	15·32	1·259	12·17
N ₂	34·33	3·037	11·30
CO	34·44	3·037	11·34
NO	36·24	3·107	11·66
O ₂	36·55	3·175	11·51

The decrease in the coefficient of absorption with rise of temperature must be connected with a change in the physical properties of the water. Winkler (1891) observed a certain relation between the internal friction and the coefficient of absorption at various temperatures.

dissolved varies directly with the pressure. This rule is called the **law of Henry and Dalton**, and is applicable to those gases which are slightly soluble in water. Therefore in a vacuum a gas becomes separated from its solution in water, and water saturated with a gas under great pressure parts with it if the pressure is diminished. For instance, many mineral springs are saturated underground with carbonic anhydride under the great pressure of the column of water above them. On coming to the surface, the water of these springs boils and foams on giving up the excess of dissolved gas. Sparkling wines and aërated waters are saturated under pressure with the same gas. They retain the gas so long as they are kept in a well-corked vessel. When the cork is removed, and the liquid comes into contact with air at a lower pressure, part of the gas, unable to remain in solution at a lower pressure, is separated as froth with the hissing sound familiar to all. It must be remarked that the law of Henry and Dalton belongs to the class of *approximate laws*, like the laws of gases (Gay-Lussac's and Mariotte's)—that is, it expresses only a portion of a complex phenomenon or the limit towards which the phenomenon tends. The matter is rendered complicated by the influence exerted by the degree of solubility and by the affinity of the dissolved gas for water. Gases which are little soluble—for instance, hydrogen, oxygen, and nitrogen—follow the law of Henry and Dalton the most closely. Carbonic anhydride exhibits a decided deviation from the law (Wroblewski, 1882); at 0° a cubic centimetre of water absorbs 1.8 cubic centimetre of the gas under a pressure of one atmosphere; under 10 atmospheres, 16 cubic centimetres (and not 18, as it should be according to the law); under 20 atmospheres, 26.6 cubic centimetres (instead of 36); and under 30 atmospheres, 33.7 cubic centimetres.³¹ However, as is shown by the researches of Sechenoff, the absorption of carbonic anhydride within certain limits of change of pressure, and at the ordinary temperature, by water—and even by solutions of salts which are not chemically changed by

³¹ These figures show that the coefficient of solubility decreases with an increase of pressure, notwithstanding that the carbonic anhydride approaches more nearly to a liquid state. As a matter of fact, liquefied carbonic anhydride does not mix with water. This indicates, in the first place, that solution does not consist in liquefaction, and in the second place that the solubility of a substance is determined by a peculiar attraction of water for the substance dissolving. Wroblewski even considered it possible to admit that a dissolved gas retains its properties as a gas. This he deduced from experiments showing that the rate of diffusion of gases in a solvent is, for gases of different densities, inversely proportional to the square roots of their densities, as is the case with the velocities of gaseous molecules (see note 34). Wroblewski demonstrated the affinity of water, H_2O , for carbonic anhydride, CO_2 , by showing that on expanding moist carbonic anhydride, compressed at 0° under a pressure of 10 atmospheres (a fall in temperature takes place from the expansion), a very unstable definite crystalline compound, $\text{CO}_2 + 8\text{H}_2\text{O}$, is obtained.

it, or do not form compounds with it—follows very closely the law of Henry and Dalton, the chemical bond between this gas and water being so feeble that the breaking up of the solution with separation of the gas is accomplished by a decrease of pressure alone.³² The case is different if a considerable affinity exists between the dissolved gas and the water. It might then be even expected that the gas would not be entirely separated from water in a vacuum, as should be the case with gases following the law of Henry and Dalton. As examples, ammonia and hydrochloric acid gas may be taken. The former is separated by boiling and decrease of pressure, while the latter is not; but they both deviate distinctly from the law.

Pressure in mm. of mercury	Ammonia dissolved in 100 grams of water at 0°	Hydrochloric acid gas dissolved in 100 grams of water at 0°
	Grams	Grams
100	28.0	65.7
500	69.2	78.2
1,000	112.6	85.6
1,500	165.6	—

It will be remarked, for instance, from this table that, whilst the pressure increases ten times, the solubility of ammonia only increases 4 times.

A number of examples might be cited of cases of the absorption of gases by liquids which do not in any way, even approximately, agree with the law of Henry and Dalton. Thus, for instance, carbonic anhydride is absorbed by a solution of caustic potash in water, and if sufficient caustic potash be present the gas will not be evolved from the solution by decreasing the pressure. This is a case of more intimate chemical combination. A correlation less patent, but similar and clearly chemical, appears in certain cases of the solution of gases in water, and we shall afterwards find an example of this in the solution of hydrogen iodide; but we will first stop to consider a remarkable application of the law of Henry and Dalton³³ to the case of the solution

³² As, according to the researches of Roscoe and his collaborators, ammonia exhibits a considerable deviation at low temperatures from the law of Henry and Dalton, whilst at 100° the deviation is small, it would appear that the dissociating influence of temperature affects all gaseous solutions; that is, at high temperatures the solutions of all gases will follow the law, whilst at lower temperatures there will in all cases be a deviation from it.

³³ The ratio between the pressure and the amount of gas dissolved was discovered by Henry in 1805, while Dalton in 1807 pointed out the applicability of this law to cases of gaseous mixtures, introducing the conception of partial pressures which is absolutely necessary for a right comprehension of Henry's law. The conception of partial pressures enters essentially into that of the diffusion of vapours in gases (footnote 1); for the

of a mixture of two gases, this being all the more necessary because the phenomena which there take place cannot be foreseen without a clear theoretical representation of the nature of gases.³⁴

pressure of damp air is equal to the sum of the pressures of dry air and of the aqueous vapour in it, and it is admitted as a corollary to Dalton's law that evaporation in dry air takes place as in a vacuum. It is, however, necessary to remark that the volume of a mixture of two gases (or vapours) is only approximately equal to the sum of the volumes of its constituents (the same, naturally, also refers to their pressures)—that is to say, in mixing gases a change of volume occurs, which, although small, is quite apparent when carefully measured. For instance, in 1888 Brown showed that on mixing equal volumes of sulphurous anhydride (SO_2) and carbonic anhydride (at the same pressure—760 mm.—and temperature) a decrease of pressure of 3.9 millimetres of mercury takes place. The possibility of chemical action in such mixtures is evident from the fact that equal volumes of sulphurous and carbonic anhydrides at -19° form, according to Pictet's researches in 1888, a liquid which may be regarded as an unstable chemical compound, or as a solution similar to that given when sulphurous anhydride and water combine to an unstable chemical whole.

³⁴ The origin of the now generally accepted **kinetic theory of gases**, according to which their molecules are animated by a rapid progressive motion, is very ancient (Bernouilli and others in the last century had already developed a similar representation), but it was only generally accepted after the mechanical theory of heat had been established, and after the work of Krönig (1855), and especially after its mathematical side had been worked out by Clausius and Maxwell. The pressure, elasticity, diffusion, and internal friction of gases, the laws of Boyle, Mariotte, and of Gay-Lussac and Avogadro-Gerhardt are not only explained (deduced) by the kinetic theory of gases, but also expressed with perfect exactitude; thus, for example, the magnitude of the internal friction of different gases was foretold with exactitude by Maxwell by applying the theory of probabilities to the impact of gaseous particles. The kinetic theory of gases must therefore be considered as one of the most brilliant acquisitions of the latter half of the nineteenth century. The velocity of the progressive motion of the particles of a gas, one cubic centimetre of which weighs d grams, is found, according to the theory, to be equal to the square root of the product of $3p \cdot D \cdot g$ divided by d , where p is the pressure under which d is determined expressed in centimetres of the mercury column, D the weight of a cubic centimetre of mercury in grams ($D=13.59$, $p=76$; consequently the normal pressure = 1,033 grams on a sq. cm.), and g the acceleration of gravity in centimetres ($g=980.5$ at the sea level and lat. 45° and 981.92 at St. Petersburg; in general it varies with the latitude and altitude of the locality). Therefore at 0° the velocity of hydrogen is 1,843, and that of oxygen 461, metres per second. This is the average velocity, and (according to Maxwell and others) it is probable that the velocities of individual particles are different; that is, they occur, as it were, in different conditions of temperature, which it is very important to take into consideration in investigating many phenomena proper to matter. It is evident from the above determination of the velocity that different gaseous molecules, at the same temperature and pressure, have average velocities inversely proportional to the square roots of their densities: this is also shown by direct experiment on the flow of gases through a fine orifice, or through a porous wall. This *dissimilar velocity of flow* for different gases is frequently taken advantage of in chemical researches (see Chap. II. and also Chap. VII.) in order to separate two gases having different densities and velocities. The difference of the velocity of flow of gases also determines the phenomenon cited in the following footnote for demonstrating the existence of an internal motion in gases.

If for a certain mass of a gas which follows exactly the laws of Mariotte and Gay-Lussac the temperature t and the pressure p be changed simultaneously, then the entire change would be expressed by the equation $pv=C(1+\alpha t)$, or, what is the same, $pv=RT$, where $T=t+273$ and C and R are constants which vary not only with the units taken but also with the nature of the gas and its mass. But as there are

The law of partial pressures is as follows:—The solubility of gases mixed with each other does not depend on the influence of the total pressure acting on the mixture, but on the influence of that portion of the total pressure which is due to the volume of each separate gas in the mixture. Thus, for instance, if oxygen and carbonic anhydride were mixed in equal volumes and exerted a pressure of 760 millimetres, then water would dissolve as much of each of these gases as would be dissolved if each separately exerted a pressure of half an atmosphere, and in this case, at 0°, one cubic centimetre of water would dissolve 0.90 cubic centimetre of carbonic anhydride. If the pressure of a gaseous mixture equal h , and in n volumes of the mixture there be a volumes of a given gas, then its solution will proceed as though this gas were dissolved under a pressure $\frac{h \times a}{n}$. That portion of the pressure under the influence of which the solution proceeds is termed the 'partial' pressure.

In order to clearly understand the cause of the law of partial pressures, an explanation must be given of the fundamental properties of gases according to the views of contemporary science. Gases are elastic and disperse in all directions. We are led, from what we know of gases, to the assumption that these fundamental properties are due to a rapid progressive motion, in all directions, proper to the smallest particles (molecules) of the gases.³⁵ These molecules in impinging against

discrepancies from both the fundamental laws of gases (which will be discussed in the following chapter), and as, on the one hand, a certain attraction between the gaseous molecules must be assumed, while, on the other hand, the molecules of gases themselves must occupy a certain portion of space, hence for ordinary gases, within any considerable variation of pressure and temperature, recourse should be had to **van der Waals' formula**—

$$\left(p + \frac{a}{v^2} \right) (v - b) = R (1 + \alpha t),$$

where α is the coefficient of expansion of gases.

The formula of van der Waals has an especially important significance in the case of the passage of a gas into the liquid state, because the fundamental properties of both gases and liquids are equally well expressed by it, although only in their general features.

The further development of the questions referring to the subjects here touched upon, which are of especial interest for the theory of solutions, must be looked for in special memoirs and works on theoretical and physical chemistry. A small part of this subject will be partially considered in the footnotes of the following chapter.

³⁵ Although the actual motion of gaseous molecules, which is accepted by the kinetic theory of gases (note 34), cannot be seen, yet its existence may be rendered evident by taking advantage of the difference in the velocities, undoubtedly belonging to different gases which are of different densities, under equal pressures. The molecules of a light gas must move more rapidly than the molecules of a heavier gas in order to produce the same pressure. Let us take, therefore, two gases, hydrogen and air: the former is 14.4 times lighter than the latter, and hence the molecules of hydrogen must

an obstacle produce a pressure, and the greater the number of molecules impinging against an obstacle in a given time, the greater the pressure. The pressure of a separate gas or of a gaseous mixture depends on the sum of the pressures of all the molecules—on the number of blows in a unit of time on a unit of surface, and on the mass and velocity (or the *vis viva*) of the impinging molecules. The nature of the different molecules is of no account; the obstacle is acted on by a pressure due to their total *vis viva*. But in a chemical action such as the solution of gases, the nature of the impinging molecules plays, on the contrary, a most important part. In impinging against a liquid, a portion of the gas enters into the liquid itself, and is held by it so long as other gaseous molecules impinge against the liquid, that is, exert a pressure on it. As regards the solubility of a given gas, for the number of blows it makes on the surface of a liquid, it is immaterial whether other molecules of gases impinge side by side with it or not. Hence, the solubility of a given gas will be proportional, not to the total pressure of a gaseous mixture, but to that portion of it which is due to the given gas separately. Moreover, the saturation of a liquid by a gas depends on the fact that the gaseous molecules that have entered the liquid do not remain at rest in it—although they enter into an harmonious kind of motion with the molecules of the liquid—but throw themselves off from its surface (just like the vapour of a volatile liquid). If in a unit of time an equal number of molecules penetrate into (leap into) and leave (or leap out of) a liquid, it is saturated. It is in a condition of mobile equilibrium, and not of rest. Therefore, if the pressure be diminished, the number of molecules departing from the liquid will exceed the number of molecules entering into the liquid, and a fresh state of mobile equilibrium only takes place on the attainment of a fresh equality between the number of molecules departing from and entering the liquid. In this manner are explained the main features of solution, and furthermore of that special (chemical) attraction

move almost four times more quickly than air (more exactly 3·8). Consequently, if a porous cylinder containing air is introduced into an atmosphere of hydrogen, then, in a given time, the volume of hydrogen which succeeds in entering the cylinder will be greater than the volume of air leaving the cylinder, and therefore the pressure inside the cylinder will rise until the gaseous mixture (of air and hydrogen) attains an equal density both inside and outside of the cylinder. If now the experiment be reversed and air surround the cylinder, and hydrogen be inside the cylinder then more gas will leave than enter the cylinder, and hence the pressure inside the cylinder will be diminished. In these considerations we have replaced the idea of the number of molecules by the idea of volumes. We shall learn subsequently that equal volumes of different gases contain the same number of molecules (the law of Avogadro-Gerhardt), and therefore instead of speaking of the number of molecules we can speak of the number of volumes. If the cylinder be partially immersed in water the rise and fall of the pressure can be observed directly, and the experiment consequently rendered self-evident.

(penetration and harmonious motion) of a gas for a liquid which determines both the measure of the solubility and the degree of stability of the solution produced.

The consequences of the law of partial pressures are exceedingly numerous and important. In nature all liquids are in contact with the atmosphere, which, as we shall afterwards see more fully, consists of a mixture of gases, chiefly four in number—oxygen, nitrogen, carbonic anhydride, and aqueous vapour. A hundred volumes of air contain, approximately, 78 volumes of nitrogen and about 21 volumes of oxygen; the quantity of carbonic anhydride, by volume, does not exceed 0.05. Under ordinary circumstances, the amount of aqueous vapour is much greater than this, but it varies with climatic conditions. We conclude from these numbers that the solution of nitrogen in a liquid in contact with the atmosphere will proceed under a partial pressure of $\frac{78}{100} \times 760$ mm. (if the atmospheric pressure equal 760 mm.), that is, under a pressure of 600 mm. of mercury; whilst the solution of the oxygen will proceed under a partial pressure of about 160 mm., and the solution of the carbonic anhydride under the very small pressure of 0.4 mm. As, however, the solubility of oxygen in water is twice that of nitrogen (note 30), the ratio of oxygen to nitrogen dissolved in water will be greater than the ratio in air. It is easy to calculate what quantity of each of the gases will be contained in water, and taking the simplest case we will calculate what quantities of these gases will be dissolved from air containing 21 per cent. of oxygen and 79 per cent. of nitrogen at 0° and 760 mm. pressure. Under a pressure of 760 mm., 1 cubic centimetre of water dissolves 0.0235 cubic centimetre of nitrogen, and under the partial pressure of 600 mm. it will dissolve $0.0235 \times \frac{600}{760}$, or 0.0185 cubic centimetre; of oxygen, $0.0482 \times \frac{160}{760}$, or 0.0102 cubic centimetre, will be dissolved. Hence 100 cubic centimetres of water will contain at 0° altogether 2.87 cubic centimetres of atmospheric gases, containing about 65 per cent. of nitrogen and 35 per cent. of oxygen by volume—i.e., about $\frac{1}{3}$ by volume of oxygen, although in the atmosphere this gas only occupies $\frac{1}{5}$ by volume.^{35a}

According to the law of partial pressures, whatever gas be dissolved in water will be expelled from the solution in an atmosphere of another gas. This depends on the fact that gases dissolved in water escape from it in a vacuum, because the pressure is nil, and an atmosphere of another gas acts like a vacuum towards a gas dissolved in water.

^{35a} The amount of carbonic anhydride held (dissolved) in river water is usually greater than the amount obtained by calculation from its content in air. This is due to the oxidation of organic matter and to the exhalations of the fish, &c., in the water, with the consequent formation of carbonic anhydride.

Evolution of gas then proceeds, because molecules of the dissolved gas no longer impinge upon the liquid, and are therefore not dissolved in it, and those previously held in solution leave the liquid in virtue of their elasticity.³⁶ For the same reason a gas may be entirely expelled from a gaseous solution by boiling—at least, in many cases, when it does not form particularly stable compounds with water. In fact, on the surface of the boiling liquid there will be aqueous vapour, and therefore all the pressure acting on the gas will be due to the aqueous vapour. On this account the partial pressure of the dissolved gas will be very inconsiderable, and this is the sole reason why *a gas separates from solution on boiling the liquid containing it*. At the boiling-point of water the solubility of gases in water is still sufficiently great for a considerable quantity of a gas to remain in solution. The gas dissolved in the liquid is carried away, together with the aqueous vapour, and if boiling be continued for a long time, all the gas will finally be given up.³⁷

³⁶ Here two cases occur: either the atmosphere surrounding the solution may be limited, or it may be proportionally so vast as to be unlimited, like the earth's atmosphere. If a gaseous solution be brought into an atmosphere of another gas which is limited—for instance, as in a closed vessel—then a portion of the gas held in solution will be expelled, and thus pass over into the atmosphere surrounding the solution, and will produce its partial pressure, under the influence of which a portion of the gas will remain in solution. But where the atmosphere into which the gaseous solution is introduced is not only that of another gas but also unlimited, then the gas dissolved will, on passing out from the solution, diffuse into this atmosphere, and produce an infinitely small pressure in the unlimited atmosphere. Consequently, no gas can be retained in solution under this infinitely small pressure, and it will be entirely expelled from the solution. For this reason water saturated with a gas which is not contained in air, will be entirely deprived of the dissolved gas if left exposed to the air. Water also passes off from a solution into the atmosphere, and it is evident that there might be such a case as a constant proportion between the quantity of water vaporised and the quantity of a gas expelled from a solution, so that not the gas alone, but the entire gaseous solution, would pass off. A similar case to this is met with in solutions which are not decomposed by heat (such as those of hydrogen chloride and iodide), as will afterwards be considered.

³⁷ However, in those cases where the variation of the coefficient of solubility with the temperature is not sufficiently great, and where certain quantities of aqueous vapour and gas pass off from a solution at the boiling-point, an atmosphere may be obtained having the same composition as the liquid itself. In this case the amount of gas passing over into such an atmosphere will not be greater than that held by the liquid, and therefore such a gaseous solution will distil over unchanged. The solution will then represent, like a solution of hydriodic acid in water, a liquid which is not altered by distillation, while the pressure under which this distillation takes place remains constant. Thus, in all its aspects, solution presents gradations from the most feeble affinity to intimate chemical combination between the solvent and dissolved substance. The **amount of heat** evolved in the solution of equal volumes of different gases stands in direct relation to these variations of stability and solubility of the gases. 22.3 litres of the following gases (at 760 mm. pressure) evolve the following numbers of (gram) units of heat on dissolving in a large mass of water; carbonic anhydride 5,600; sulphurous anhydride 7,700; ammonia 8,800; hydrochloric acid 17,400; and hydriodic acid 19,400. The last two gases, which are not expelled from their solutions by boiling, evolve approximately twice as

It is evident that the conception of the partial pressures of gases should be applied not only to the formations of solutions, but also to all cases of chemical action of gases. Especially numerous are its applications to the physiology of respiration, for in these cases it is only the oxygen of the atmosphere that acts.³⁸

The solution of **solids**, while depending in a small measure on the pressure under which solution takes place (because solids and liquids are almost incompressible), is very often greatly dependent on the temperature. In the majority of cases the solubility of solids in water increases as the temperature rises; and, further, the rapidity of solution increases also. The latter is determined by the rapidity of diffusion of the solution formed into the remainder of the water. The solution of a solid in water, although it is, as with gases, a physical change into a liquid state, is determined by its chemical affinity for water: this is clearly shown from the fact that in solution there occurs a diminution in volume, changes in the boiling-point of the water, in the pressure of its vapour, in the freezing point, and in many similar properties. If solution were a physical, and not a chemical, phenomenon, it would naturally be accompanied by an increase and not by a diminution of volume, because, in melting, solids generally increase in volume (their density diminishes). **Contraction** is the usual phenomenon accompanying solution, and takes place even on the addition of solutions to water,³⁹

much heat as gases like ammonia, which are separated from their solutions by boiling, whilst gases which are only slightly soluble evolve very much less heat.

³⁸ With regard to the numerous researches treating of this subject, certain results obtained by Paul Bert are cited in Chapter III., and we will here point out that Prof. Sechenoff, in his researches on the absorption of gases by liquids, investigated very fully the phenomena of the solution of carbonic anhydride in solutions of various salts, and arrived at many important results, which showed that, on the one hand, in the solution of carbonic anhydride in solutions of salts on which it is capable of acting chemically (for example, sodium carbonate, borax, ordinary sodium phosphate), there is not only an increase of solubility, but also a distinct deviation from the law of Henry and Dalton; whilst, on the other hand, solutions of salts which are not acted on by carbonic anhydride (for example, the chlorides, nitrates, and sulphates) absorb less of it, owing to the 'competition' of the salt already dissolved, and follow the law of Henry and Dalton, but at the same time show undoubted signs of a chemical action between the salt, water, and carbonic anhydride. Sulphuric acid (whose coefficient of absorption is 92 vols. per 100), when diluted with water, absorbs less and less carbonic anhydride, until the hydrate $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ is formed, when the coefficient of absorption equals 66 vols.; then, on further addition of water, the solubility again rises.

³⁹ Kremers made this observation in the following simple way:—He took a narrow-necked flask with a mark on the narrow part (like that on a litre flask used for accurately measuring liquids), poured water into it, and then inserted a funnel, having a fine tube which reached to the bottom of the flask. Through this funnel he carefully poured a solution of any salt, and (having removed the funnel) allowed the liquid to attain a definite temperature (in a water-bath); he then filled the flask up to the mark with water. In this manner two layers of liquid were obtained, the heavy saline solution below and water above. The flask was then shaken in order to accelerate diffusion, and

and on the solution of liquids in water,⁴⁰ just as happens in the combination of substances with the production of chemically new substances.⁴¹ The contraction which takes place in solution is, however, very small; a fact which depends on the small compressibility of solids and liquids, and on the insignificance of the compressing force acting in solution.⁴² The change of volume which takes place in the solution of solids and liquids, or the alteration in specific gravity⁴³ and many other physical properties corresponding with it, depends on

it was observed that the volume became less if the temperature remained constant. This can be proved by calculation, if the specific gravity of the solutions and water be known. Thus at 15°, 1 c.c. of a 20 per cent. solution of common salt weighs 1.1500 gram, so that 100 grams of it occupy a volume of 86.96 c.c. As the sp. gr. of water at 15° is 0.99916, 100 grams of water occupy a volume of 100.08 c.c. The sum of the volumes is 187.04 c.c. After mixing, 200 grams of a 10 per cent. solution are obtained. Its specific gravity is 1.0725 (measured at 15° and referred to water at its maximum density); hence the 200 grams will occupy a volume of 186.48 c.c. The contraction is consequently equal to 0.56 c.c.

⁴⁰ The contractions produced in the case of the solution of sulphuric acid in water are shown in the diagram, fig. 17 (page 74). The maximum is 10.1 c.c. per 100 c.c. of the solution formed. A maximum contraction of 4.15 at 0°, 3.78 at 15°, and 3.50 at 30° takes place on dissolving 46 parts by weight of anhydrous alcohol in 54 parts of water. This signifies that if, at 0°, 46 parts by weight of alcohol be taken and 54 parts by weight of water, then the sum of their separate volumes will be 104.15, whilst after mixing their total volume will be 100.

⁴¹ This subject will be considered later in this work, and we shall then see that the contraction produced in reactions of combination (of solids or liquids) is very variable in its amount, and that there are, although rarely, reactions of combination in which contraction does not take place, or when an increase of volume is produced. Solutions exhibit a similar phenomenon.

⁴² The compressibility of solutions of common salt is less, according to Grassi, than that of water. At 18° the compression of water is 48 vols. per million for a pressure of one atmosphere; for a 15 per cent. solution of common salt it is 32, and for a 24 per cent. solution 26 vols. Similar determinations were made by Brown (1887) for saturated solutions of sal-ammoniac (38 vols.), alum (46 vols.), common salt (27 vols.), and sodium sulphate at + 1°, when the compressibility of water is 47 per million volumes. This investigator also showed that substances which dissolve with an evolution of heat and with an increase in volume (as, for instance, sal-ammoniac) are partially separated from their saturated solutions by an increase of pressure (this experiment was particularly conclusive in the case of sal-ammoniac), whilst the solubility of substances which dissolve with an absorption of heat or diminution in volume increases, although very slightly, **with an increase of pressure**. Sorby observed the same phenomenon with common salt (1863).

⁴³ The most trustworthy data relating to the variation of the specific gravity of solutions with a change of their composition and temperature are collected and discussed in my work cited in footnote 19. The practical (the amount of a substance in solution being determined by the aid of the specific gravities of solutions, both in works and in laboratory practice) and the theoretical (for specific gravity can be more accurately observed than other properties, and because a variation in specific gravity governs the variation of many other properties) interest of this subject, besides the strict rules and laws to which it is liable, make one wish that this province of data concerning solutions may soon be enriched by further observations of as accurate a nature as possible. Their carrying out does not present any great difficulty, although requiring much time and attention.

peculiarities of the dissolving substances and of water, and, in the majority of cases, is not proportional to the quantity of the substance dissolved,⁴⁴ showing the existence of a chemical force between the solvent and the substance dissolved, which is of the same nature as in all other forms of chemical reaction.⁴⁵

⁴⁴ Owing to the degree of change, exhibited in many properties on the formation of solutions, not being large, and to the insufficient accuracy of observations, a proportionality between this change and change of composition may, especially within narrow limits of change of composition, easily be imagined in cases where it does not exist. The conclusion of Michel and Kraft is particularly instructive in this respect; in 1854, on the basis of their researches, they assumed that the increment of the specific gravity of solutions was proportional to the increment of salt in a given volume of a solution, which is only true for determinations of specific gravity exact merely to the second decimal place—an accuracy insufficient even for technical determinations. Accurate measurements do not confirm a proportionality either in this case or in many others where such has been generally accepted; as, for example, in the rotatory power (of the plane of polarisation) of solutions, and in their capillarity, &c. Judging by the results obtained in my researches on the specific gravity of solutions, I think that in many cases it would be nearer the truth to take the change of properties as proportional, not to the amount of a substance dissolved, but to the product of this quantity and the amount of water in which it is dissolved; the more so since many chemical relations vary in proportion to the reacting masses, and a similar ratio has been established for many phenomena of attraction studied by mechanics.

⁴⁵ All the different forms of chemical reaction may be said to take place in the process of solution: (1) *Combinations* between the solvent and the substance dissolved, yielding compounds more or less stable (more or less dissociated). This form of reaction is the most likely to occur, and is that most often observed. (2) Reactions of *substitution* or of *double decomposition* between the molecules. Thus it may be supposed that in the solution of sal-ammoniac, NH_4Cl , the action of water produces ammonia, NH_4HO , and hydrochloric acid, HCl , which are dissolved in the water and simultaneously attract each other. As these solutions and many others do indeed exhibit signs, sometimes indisputable, of such double decompositions (thus solutions of sal-ammoniac yield a certain amount of ammonia), it is probable that this form of reaction is more often met with than is generally thought. (3) *Isomeric changes* also probably take place in solution, all the more so since here molecules of different kinds come into intimate contact, and it is very likely that under these influences the configuration of the atoms in the molecules is somewhat different from what it was in its original and isolated state. One is led to this supposition especially from observations made on solutions of substances which rotate the plane of polarisation (and observations of this kind are very sensitive with respect to the atomic structure of molecules), because they show, for example (according to Schneider, 1881), that strong solutions of malic acid rotate the plane of polarisation to the right, whilst its ammonium salts in all degrees of concentration rotate to the left. (4) Reactions of *decomposition* under the influences of solution are not only rational in themselves, but have in recent years been recognised by Arrhenius, Ostwald, and others, particularly on the basis of electrolytic determinations. If some of the molecules of a solution occur in a condition of decomposition, the rest may occur in a still more complex state of combination, just as the velocities of different gaseous molecules may be far from being the same (see note 34).

It is, therefore, very probable that the reactions taking place in solution vary both quantitatively and qualitatively with the mass of water in the solution, and the great difficulty of arriving at a definite conclusion as to the nature of the chemical relations in solution will be understood; and as also the existence of a physico-mechanical process like the sliding between and interpenetration of two homogeneous liquids must also be recognised in solution, the complexity of the problem as to the actual nature of solutions,

The feeble development of the chemical affinities acting in solutions of solids becomes evident on considering the different methods by which **their solutions are decomposed**, with the separation of either their component parts or their definite compounds with water. The water contained in solutions is removed from them as vapour, or, by freezing, in the form of ice,⁴⁶ but **the pressure of the vapour of the water**⁴⁷ present in a solution is less than that of water in a free state, and the **temperature of the formation of ice** from solutions is lower than 0° . Further, both the diminution of vapour pressure and the lowering of the freezing-point are, in dilute solutions, very nearly proportional to the amount of a substance dissolved.⁴⁸ Thus, if for every 100 grams of water there be in solution 1, 5, or 10 grams of common salt (NaCl), then at 100° the vapour pressure of the solution will be 4, 21, or 43 mm. less than 760 mm.—the vapour pressure of water—while the freezing-points are -0.58° , -2.91° , and -6.10° respectively. The above figures⁴⁹ are almost proportional to the amounts

which is now to the fore, appears in its true light. But it would not be expedient to discuss this complex subject and the numerous researches upon it in a short exposition of the principles of chemistry. It requires to be specially and fully treated in physical chemistry (see Chapter VII., note 27).

⁴⁶ In separating as ice or vapour, water makes, with a solution, a heterogeneous system (made up of substances in different physical states) similar, for instance, to the formation of a precipitate or volatile substance in reactions of double decomposition.

⁴⁷ If the substance dissolved is non-volatile (like salt or sugar), or only slightly volatile, then the whole of the pressure of the vapour given off is due to the water; but if a solution of a volatile substance—for instance, a gas or a volatile liquid—evaporates, then only a portion of the pressure belongs to the water, and the whole pressure observed consists of the sum of the pressures of the vapours of the water and of the substance dissolved. The majority of researches bear on the first case, which will be spoken of presently, whilst the observations of D. P. Konovaloff (1881) refer to the second case. He showed that in the case of two volatile liquids, mutually soluble in each other, forming two layers of saturated solutions (for example, ether and water, note 20, p. 65), both solutions have an equal vapour pressure in the case in point the pressure of each is equal to 431 mm. of mercury at 19.8°). Further, he found that for solutions which are formed in all proportions, the pressure is either greater (solutions of alcohol and water) or less (solutions of formic acid) than that corresponding with the rectilinear change (proportional to the composition) from the pressure of water to the pressure of the substance dissolved; thus the pressure, for example, of a 70 per cent. solution of formic acid is less, at all temperatures, than the pressure of water or that of formic acid. In this case the pressure of a solution is never equal to the sum of the pressures of the dissolving liquids, as Regnault already showed when he distinguished this case from that in which a mixture of liquids, which are insoluble in each other, evaporates. From this it is evident that a mutual action occurs in solution, which diminishes the vapour pressure proper to the individual substances, as would be expected on the supposition of the formation of compounds in solutions, because the elasticity then always diminishes.

⁴⁸ This amount is usually expressed by the weight of the substance dissolved per 100 parts by weight of water. Probably it would be better to express it by the quantity of the substance in a definite volume of the solution—for instance, in a litre—or by the ratio of the numbers of molecules of water and of the dissolved substance.

⁴⁹ The variation of the vapour pressure of solutions has been the subject of many

of salt in solution (1, 5, and 10 per 100 of water). Furthermore, it has investigations. The best known researches are those of Wüllner in Germany (1858–1860) and of Tamman in Russia (1887). The researches on the temperature of the formation of ice by various solutions are also very numerous; Blagden (1788), Rüchdorff (1861), and De Coppet (1871) were the first to start such work, which, however, takes its chief interest from the work of Raoult, begun in 1882 on aqueous solutions, and afterwards continued with solutions in various other easily frozen liquids—for instance, benzene, C_6H_6 (melts at 4.96°), acetic acid, $C_2H_4O_2$ (16.75°), and others. Especial interest is attached to these **cryoscopic** investigations made by Raoult, in France, on the *depression* of the freezing-point, because he took solutions of many well-known carbon-compounds and discovered a simple relation between the molecular weights of the substances and the temperatures of crystallisation of the solvent, which enabled this method of research to be applied to the investigation of the nature of substances. We shall meet with the application of this method later on (see also Chapter VII.), and at present will only cite the deduction arrived at from these results. The solution of one-hundredth part of that molecular gram weight which corresponds with the formula of a substance (for example, $NaCl = 58.5$, $C_2H_6O = 46$, &c.) in 100 parts of a solvent lowers the freezing-point of water 0.185° , of benzene 0.49° , and of acetic acid 0.39° or twice as much as with water. And as in dilute solutions the depression or fall of freezing-point is proportional to the amount of the substance dissolved, the fall of freezing-point for all other solutions may be calculated by means of this rule. Thus, for instance, the weight which corresponds with the formula of acetone, C_3H_6O , is 58; solutions containing 2.42, 6.22, and 12.35 grams of acetone per 100 grams of water form ice (according to the determinations of Beckmann) at -0.770° , -1.930° , and -3.820° , and these figures show that with a solution containing 0.58 gram of acetone per 100 of water the fall of the temperature of the formation of ice will be 0.185° , 0.180° , and 0.179° . It must be remarked that the law of proportionality between the fall of temperature of the formation of ice and the concentration of a solution is in general only approximate, and is only applicable to weak solutions (Pickering and others).

We may here remark that the theoretical interest of this subject was strengthened on the discovery of the connection existing between the fall of vapour pressure, the depression of the temperature of the formation of ice, the diminution of osmotic pressure (van't Hoff, note 19), and the electrical conductivity of solutions, and we shall therefore supplement what we have already said on the subject by some short remarks on the method of cryoscopic investigations, although the details of the matter form the subject of more special works on physical chemistry.

In order to determine the **temperature of the formation of ice** (or of crystallisation of other solvents), a solution of known strength is prepared and poured into a cylindrical vessel surrounded by a second similar vessel, leaving between the two a layer of air which, being a bad conductor, prevents any rapid change of temperature. Still better results are obtained if the air be exhausted from the space between the two vessels and the sides of both be silvered. The transfer of heat then proceeds very slowly. The bulb of a sensitive and corrected thermometer is immersed in the solution, and also a bent platinum wire for stirring the solution; the whole is then cooled (by immersing the apparatus in a freezing mixture), and the temperature at which ice begins to separate observed. The temperature may fall slightly below its final value, but it rises and remains constant when ice begins to form. By then allowing the liquid to become slightly warmer, and again observing the temperature of the formation of ice, an exact determination may be arrived at. It is still better to take a large mass of solution, and induce the formation of the first crystals by dropping into the solution, already partially over-cooled, a small lump of ice, which only imperceptibly changes the composition of the solution. The observation should be made at the point of formation of only a very small amount of crystals, as otherwise the composition of the solution will become altered owing to their separation. Every precaution must be taken to prevent the access of moisture to the interior of the apparatus, as this might also alter the composition of the solution or the properties of the solvent (for instance, when using acetic acid).

been shown by experiment that the ratio of the diminution of vapour

With respect to the depression of dilute solutions it is known: (1) That the depression increases in almost direct proportion to the amount of the substance in solution (always per 100 parts of water); for example, for KCl when the solution contains 1 part of salt (per 100 parts of water) the depression is 0.45° , when it contains 2 parts of salt, 0.90° , or with 10 parts of salt, 4.4° . (2) The greater the molecular weight expressed by the formula (see Chapter VII.), and designated by M , the less, under similar conditions, will be the depression d , and therefore if the concentration of a solution (the amount by weight of substance dissolved per 100 parts of water) be designated by p , then the fraction $M \frac{d}{p}$ or the molecular depression for a given class of substances will be a constant quantity; for example, in the case of methyl alcohol in water 17.3 , for acetone about 18.0 , and for sugar about 18.5 . (3) In general the molecular depression for substances whose solutions do not conduct an electric current is about 18.5 , while for acids, salts, and such like substances whose solutions do conduct electricity, it is i times greater; for instance, for HCl, KI, HNO_3 , KHO, &c., about 36 (i being nearly 2), for borax about 66 , and so on, i varying in the same manner as it does in the case of the osmotic pressure of solutions (note 19). (4) Different solvents (water, acetic acid, benzene, &c.) have each their corresponding constants of molecular depression (which have a certain remote connection with their molecular weight); for example, for acetic acid the molecular depression is about 39 and not 19 (as it is for water); for benzene, 49 ; for methyl alcohol about 17 , &c. (5) If the molecular weight M of a substance be unknown, then in the case of non-conductors of electricity or for a given group, it may be found by determining the depression, d , for a given concentration, p ; for example, in the case of peroxide of hydrogen, which is a non-conductor of electricity, the molecular weight, M , was found to be nearly 34 , corresponding with the formula H_2O_2 (see Chapter VII.).

Similar results have also been found for the fall in the vapour pressure of solutions (note 51), and for the rise of their boiling-points and for other properties of the substances dissolved (Chapter VII.), and for the osmotic pressure (note 19). A variation in the magnitude of i , in passing from solutions which do not conduct an electric current to those which do conduct electricity, is everywhere remarked, so that it was natural to seek here that causal connection which Arrhenius (1888), Ostwald, and others think they have found in the supposition that a portion of the substance of the electrolyte is decomposed, in the very act of solution, into its ions (for example, NaCl into Na and Cl), or into the atoms of those individual substances which make their appearance in electrolysis, and in this way to explain the fact that i is greater for those bodies which conduct an electric current. We will not here consider this supposition, known as the hypothesis of 'electrolytic dissociation,' not merely because it belongs entirely to the special branch of physical chemistry, and gives scarcely any help towards explaining the chemical relations of solutions (particularly their passage into definite compounds, their reactions, and their very formation, but also because: (1) all the above data (for constant depression, osmotic pressure, &c.) refer only to dilute solutions, and are not applicable to strong solutions; whilst the chemical interest in strong solutions is not less than in dilute solutions, and the transition from the former to the latter is consecutive and inevitable; (2) because in any homogeneous body (although it may be insoluble and not an electrolyte) some of the atoms may always be supposed (Clausius) to be in the act of passing from one molecule to another (Chap. X. note 20), and hence in a dissociated state, but there are no reasons for believing that such a phenomenon is peculiar to the solutions of electrolytes; (3) because no essential difference is observed between the solution of electrolytes and non-conductors, although this might well be expected, according to Arrhenius's hypothesis; (4) because it is more reasonable to assume, in the act of solution, the formation of new, more complex, but unstable and easily dissociated compounds, than a decomposition even partial, of the substances taken; (5) because, if Arrhenius's hypothesis be accepted, it becomes necessary to admit the existence in solutions of free ions, like the atoms Cl or Na, without any

pressure in a given solution to the vapour pressure of water is an

apparent expenditure of the energy necessary for their disruption; and although on this supposition it can be explained why i then = 2, it is not at all clear why solutions of MgSO_4 give $i = 1$, although they also conduct an electric current; (6) because in dilute solutions, the approximative proportionality between the depression and concentration may be recognised, while admitting the formation of hydrates, with as much right as in admitting the solution of anhydrous substances, and if the formation of hydrates be recognised it is easier to assume that these are partially decomposed than to accept the breaking up into ions; (7) because the best conductors of electricity are solutions of substances like the sulphates, in which it is necessary to recognise the formation of associated systems or hydrates; (8) because the cause of electro-conductivity can be sooner looked for in this affinity and this combination of the substance dissolved with the solvent, as is seen from the facts that (D. P. Konovaloff) neither aniline nor acetic acid alone conducts an electric current, a solution of aniline in water conducts it badly (and here the affinity is very small), while a solution of aniline in acetic acid forms a good electrolyte, in which, without doubt, chemical forces are acting, bringing aniline, like ammonia, into combination with the acetic acid; and, lastly, (9) because I, together with many of the chemists of the present day, cannot regard the hypothesis of electrolytic dissociation, in the form given to it up to now by Arrhenius and Ostwald, as accounting for the sum total of the chemical data respecting solutions and dissociation in general. The hypothesis of 'electrolytic dissociation' (of the electrolytes dissolved, i.e., their splitting up on solution into imaginary ions, which, according to this hypothesis, are formed even without a current) which is lamely applied to explain the increase of the value of i , but which adds nothing to our comprehension of solutions in general, suffers, moreover, in its endeavour to penetrate into the province of ordinary chemical phenomena by affirming that reaction proceeds, as a rule, only between free ions; for instance, that in the action of AgNO_3 on NaCl , the free ions of Ag , on meeting the ions of Cl , give AgCl . The followers of the hypothesis have applied this view to a number of phenomena (such as coloration, distribution, &c.) and reactions. For my part I consider this side of the question still less satisfactory and less in accordance with fact, and in illustration of this I will cite the following two (out of many) instances. (1) Liveing (1900) showed that the absorption spectrum (see Chap. XIII.) of solutions of a certain salt of didymium remains unchanged, notwithstanding a variation in the amount of water (concentration), if only the ray of light passing through the solution encounters the same quantity of the didymium salt (for instance, if in one case A grams of salt per litre be taken and the column of solution be n centimetres long, and in another case xA grams of the salt be present per litre and the column be n/x centimetres long). But according to the followers of the electrolytic dissociation hypothesis, the more diluted the solution the greater the proportion of free ions, and the coloration and absorption spectra of solutions are determined by these free ions. (2) L. Kahlenberg (1902) showed that on mixing a solution of dry oleate of copper, $\text{Cu}x_2$ (where $x = \text{C}_{18}\text{H}_{33}\text{O}_2$), in dry benzene with a benzene solution of perfectly dry hydrochloric acid, 2HCl (non-conductors of electricity, and therefore, according to the hypothesis, containing no free ions), they immediately give a precipitate of chloride of copper, CuCl_2 , because the latter is insoluble in benzene. But according to the hypothesis of electrolytic dissociation, this could in nowise be expected, because as the above solutions do not conduct an electric current they should contain no free ions, and therefore instantaneous reaction should not take place. I do not consider the hypothesis in question to be in accordance with fact, and therefore refrain from giving a detailed exposition of it in this work. Thus, although I consider it superfluous to discuss further the evolution of the above theory of solutions, still I think that it would be most useful for students of chemistry to consider all the data referring to this subject, which can be found in the *Zeitschrift für physikalische Chemie*, first published in 1887. Besides which, I think it well to point out that in my opinion (note 45) the nature of solutions is very complex, and there is reason for recognising a portion of the substances present to be in a state of combination and another portion in a state of dissociation, having nothing in common with the still obscure

almost constant quantity at different temperatures,⁵⁰ and that for every (dilute) solution the ratio between the depressions of the vapour pressure and of the freezing-point is also a tolerably constant quantity.⁵¹

The diminution of the vapour pressure of solutions explains the rise in boiling-point occasioned by the solution of solid non-volatile bodies in water. The temperature of a vapour is the same as that of the solution from which it is generated, and therefore it follows that the aqueous vapour given off from a solution will be superheated. A saturated solution of common salt boils at 108·4°, a solution of 335 parts of nitre in 100 parts of water at 115·9°, and a solution of 325 parts of potassium chloride in 100 parts of water at 179°, if the temperature of ebullition be determined by immersing the thermometer bulb in the liquid itself. This is another proof of the bond which exists between the water and the dissolved substance. And this bond is indicated still more clearly in those cases (for example, in the solution of nitric or formic acid in water) where the solution boils at a higher temperature than either water or the volatile substance dissolved in it. For this reason the solutions of certain gases—for instance hydriodic or hydrochloric acid—boil above 100°.

The separation of ice from solutions⁵² explains both the phenomenon, well known to sailors, that the ice formed from salt water gives

force of electricity. I consider that the recognition of dissociation and association in solutions will become necessary for their right comprehension, and I think that the modern conception of electrolytic dissociation, although retarding the progress of the theory of solution, is useful in giving the motive for collecting a store of experimental data to be embraced by a true theory in the future.

⁵⁰ This fact, which was established by Gay-Lussac, Pierson, and v. Babo, is confirmed by the latest observations, and enables us to express not only the fall of pressure ($p - p'$) itself, but its ratio to the pressure of water $\left(\frac{p - p'}{p}\right)$. It is to be remarked that in the absence of any chemical action, the pressure is equal, according to the law of Dalton, to the sum of the pressures of the substances taken. Hence liquids which are insoluble in each other (for example, water and chloride of carbon) present a pressure equal to the sum of their individual pressures, and therefore such a mixture boils at a lower temperature than the more volatile liquid (Magnus, Regnault).

⁵¹ If, in the example of common salt, the fall of pressure is divided by the pressure of water, a figure is obtained which is nearly 105 times less than the magnitude of the fall of temperature of formation of ice. This correlation was theoretically deduced by Goldberg, on the basis of the mechanical theory of heat, and has been experimentally confirmed for many solutions. But here again I must refer the reader to works on physical chemistry, because it is impossible to go into all the theoretical and practical details of the subject here.

⁵² Fritzsche showed that solutions of certain colouring matters yield colourless ice, clearly proving that the water alone without any intermixture of the substance dissolved passes into a solid state, although the possibility of the admixture in certain other cases cannot be denied.

fresh water,^{52a} and also the fact that by freezing, just as by evaporation, a solution is obtained which is richer in salts than before. In cold countries this is taken advantage of for obtaining from sea water a liquor, which is then evaporated for the extraction of salt.

On the removal of part of the water from a solution (by evaporation or the separation of ice), a saturated solution should be obtained, and the solid substance dissolved should then separate out. Solutions saturated at a certain temperature should also deposit a corresponding portion of the substance dissolved if they be reduced, by cooling,⁵³ to a temperature at which the water can no longer hold in solution the quantity of the substance originally present. If this separation, by cooling a saturated solution or by evaporation, takes place slowly, **crystals** of the substance dissolved are in many cases formed; and this is the method by which crystals of soluble salts are usually obtained. Certain solids very easily separate out from their solutions in perfectly formed crystals, which may attain very large dimensions. Such are nickel sulphate, alum, sodium carbonate, chrome-alum, copper sulphate, potassium ferricyanide, and a whole series of other salts. The most remarkable circumstance in this is that many solids in separating out from an aqueous solution retain a portion of water, forming crystallised solid substances which contain water. Water which is thus retained is called **water of crystallisation**. Alum, copper sulphate, Glauber's salt, and magnesium sulphate contain such water, but neither sal-ammoniac, common salt, nitre, potassium chlorate, silver nitrate, nor sugar contains water of crystallisation in its crystals. One and the same substance may separate out from a solution with or without water of crystallisation, according to the temperature at which the crystals are formed. Thus common salt when crystallised from its solution in

^{52a} If the ice be gradually formed in a continuous mass. But if it occurs as frozen fragments, it will enclose a portion of the salt water.

⁵³ As the solubility of certain substances (for example, coniine, cerium sulphate, &c.) decreases with a rise of temperature (between certain limits—see, for example, note 24), these substances separate from their saturated solutions, not on cooling, but on heating. Thus a solution of manganese sulphate, saturated at 70°, becomes cloudy on further heating. The observation of the point at which a substance separates from its solution with a change of temperature gives an easy means of determining the coefficient of solubility, and this was taken advantage of by Prof. Alexéeff for determining the solubility of many substances. The phenomenon and method of observation are here essentially the same as in the determination of the temperature of formation of ice. If a solution of a substance which separates out on heating be taken (for example, sulphate of calcium or manganese), then on a certain fall of temperature ice will separate out from it, and on a certain rise of temperature the salt will separate out. From this example, and from general considerations, it is clear that the separation of a dissolved substance from a solution presents a certain analogy to the separation of ice from a solution. In both cases a heterogeneous system of a solid and a liquid is formed from a homogeneous (liquid) system.

water at the ordinary or at a higher temperature does not contain water of crystallisation. But if it separates from solution at a low temperature, namely, below -10° , then 100 parts of the crystals contain 38 parts of water. Crystals of the same substance which separate out at different temperatures may contain different amounts of water of crystallisation. This proves to us that a solid dissolved in water may form various compounds with it, differing in their properties and composition, and capable of appearing in a separate solid form like many ordinary definite compounds. This is indicated by the numerous properties and phenomena connected with solutions, and gives reason for thinking that there exist in solutions themselves either such compounds of the dissolved substance with the solvent or compounds similar to them, only in a liquid and partly decomposed form. Even the **colour of solutions** may often confirm this opinion. Copper sulphate forms crystals having a blue colour and containing water of crystallisation. If the water of crystallisation be removed by heating the crystals to redness, a colourless anhydrous substance—a white powder—is obtained. From this it may be seen that the blue colour belongs to the compound of the copper salt with water. Solutions of copper sulphate are all blue, and consequently they contain a compound similar to the compound formed by the salt with its water of crystallisation. Crystals of cobalt chloride when dissolved in an anhydrous liquid—like alcohol, for instance—give a blue solution; but when they are dissolved in water a red solution is obtained. Crystals from the aqueous solution, according to Professor Potilitzin, contain six times as much water ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$) for a given weight of the salt as the violet crystals ($\text{CoCl}_2 \cdot \text{H}_2\text{O}$) formed by the evaporation of an alcoholic solution.

Further light on the nature of solutions is given by supersaturated solutions, by the so-called cryohydrates, by solutions of certain acids having constant boiling-points, and by the properties of compounds containing water of crystallisation, to the consideration of which we now turn.

Supersaturated solutions exhibit the following phenomena:—On cooling a saturated solution of certain salts,⁵⁴ the excess of the solid

⁵⁴ Salts which separate out with water of crystallisation and form several crystallohydrates yield supersaturated solutions with the greatest facility, and the phenomenon is much more common than was previously imagined. The first data were given in the eighteenth century by Loewitz in St. Petersburg. Numerous researches have proved that supersaturated solutions do not differ from ordinary solutions in any of their essential properties. The variations in specific gravity, vapour pressure, formation of ice, &c., take place according to the ordinary laws, and their formation depends on the absence of solid particles (of the solid phase), about which crystallisation readily takes place (as has been partially explained in note 24).

may, under certain conditions, remain in solution and not separate out. A great number of substances, and more especially sodium sulphate, Na_2SO_4 , or Glauber's salt, readily form supersaturated solutions. If boiling water be saturated with this salt, and the *solution be poured off from any salt remaining undissolved*, and be kept boiling while the vessel containing it is well closed either with a plug of cotton wool, or by fusing it in the flame, or if the solution be covered with a layer of oil, it will be found that this saturated solution does not deposit any Glauber's salt whatever on cooling down to the ordinary or even to a much lower temperature; without, however, the above precautions, the salt separates out on cooling in the form of crystals of the composition $\text{Na}_2\text{SO}_4, 10\text{H}_2\text{O}$ —that is, containing 180 parts of water for every 142 parts of anhydrous salt. The supersaturated solution may be moved about or shaken inside the vessel holding it, and no crystallisation will take place; the salt remains in the solution in as large an amount as at a higher temperature. If the vessel holding the supersaturated solution is opened, and a crystal of Glauber's salt thrown in, crystallisation suddenly takes place.⁵⁵ A considerable rise in temperature is noticed during this rapid separation of crystals, and this is due to the fact that the salt, previously in a liquid state, passes into a solid one. This bears some resemblance to the fact that, under certain circumstances, water may be cooled below 0° (even to -10°) if it be left at rest, and then evolves heat in suddenly crystallising. Although from this point of view there is a resemblance, yet in reality the phenomenon of supersaturated solutions is much more complicated. Thus, on cooling, a saturated solution of Glauber's salt deposits crystals of the composition $\text{Na}_2\text{SO}_4, 7\text{H}_2\text{O}$,⁵⁶ and not $\text{Na}_2\text{SO}_4, 10\text{H}_2\text{O}$. The

⁵⁵ Inasmuch as air, as has been shown by direct experiment, contains, although in very small quantities, minute crystals of salts, and among them sodium sulphate, air can bring about the crystallisation of a supersaturated solution of sodium sulphate in an open vessel, but it has no effect on saturated solutions of certain other salts, for example, lead acetate. According to the observations of de Boisbaudran, Gernez, and others, isomorphous salts (analogous in composition) are capable of inducing crystallisation. Thus, a supersaturated solution of nickel sulphate crystallises by contact with crystals of other sulphates analogous with it, such as those of magnesium, cobalt, copper, and manganese. The crystallisation of a supersaturated solution, set up by the contact of a minute crystal, starts from it in rays with a definite velocity, and it is seen that the crystals as they form propagate the crystallisation in definite directions. This phenomenon recalls the evolution of organisms from germs. An attraction of similar molecules ensues, and they dispose themselves in definite similar forms.

⁵⁶ At the present time a view is very generally accepted, which regards supersaturated solutions as homogeneous systems, which pass into heterogeneous systems (composed of a liquid and a solid substance) in a manner exactly resembling the passage of water, cooled below its freezing-point, into ice and water, or the passage of crystals of rhombic sulphur into monoclinic crystals, and of the monoclinic crystals into rhombic. Although many phenomena of supersaturation are thus clearly understood, yet the spontaneous

crystals containing $7\text{H}_2\text{O}$ are distinguished for their instability : if they stand in contact not only with crystals of $\text{Na}_2\text{SO}_4, 10\text{H}_2\text{O}$, but with many other substances, they immediately become opaque, forming a mixture of the anhydrous and deca-hydrated salts. It is evident that between water and a soluble substance there may be established various kinds of more or less stable equilibrium, of which solutions form a particular case.⁵⁷

formation of the unstable hepta-hydrated salt, in the place of the more stable deca-hydrated salt, indicates that the phenomenon is essentially a complex one, and is most probably determined by the fact that chemical forces act between the water and the dissolved substance, tending to the formation of compounds of the two in different proportions and with different distribution of parts (structure). Stcherbacheff asserts, on the basis of his researches, that a solution of the deca-hydrated salt gives, on evaporation without the aid of heat, the deca-hydrated salt, whilst after heating above 33° it forms a supersaturated solution and the hepta-hydrated salt. But in order that this view should be accepted, indications must be found distinguishing solutions (which are, according to this view, isomeric) containing the hepta-hydrated salt from those containing the deca-hydrated salt, and all efforts in this direction (the study of the properties of the solutions) have given negative results. As some crystallohydrates of salts (alums, sugar of lead, calcium chloride) melt directly, without depositing anything, whilst others (like $\text{Na}_2\text{SO}_4, 10\text{H}_2\text{O}$) are broken up, it may be that the latter are in a state of equilibrium which does not persist at a temperature higher than the melting-point. It may here be observed that, on melting crystals of the deca-hydrated salt, there is formed, besides the solid anhydrous salt, a saturated solution giving the hepta-hydrated salt, so that this passage from the deca- to the hepta-hydrated salt, and the reverse, take place with the formation of the anhydrous (or, it may be, mono-hydrated) salt.

Moreover, supersaturation (Potilitzin, 1889) only takes place with those substances which are capable of giving several modifications or several crystallohydrates, i.e., supersaturated solutions deposit, besides the stable normal crystallohydrate, hydrates containing less water and also the anhydrous salt. Sulphate of nickel solution at 15° – 20° deposits rhombic crystals containing $7\text{H}_2\text{O}$, at 30° – 43° cubical crystals with $6\text{H}_2\text{O}$, at 50° – 70° monoclinic crystals, also containing $6\text{H}_2\text{O}$. The ability to deposit slightly hydrated or anhydrous salts by the introduction of a crystal into the solution is common to all supersaturated solutions. If a salt forms a supersaturated solution, then one would expect, according to this view, that it should exist in the form of several hydrates or in several modifications. Thus Potilitzin concluded that strontium chlorate, which readily gives supersaturated solutions, should be capable of forming several hydrates, besides the anhydrous salt known ; and he succeeded in discovering the existence of two hydrates, $\text{Sr}(\text{ClO}_3)_2, 3\text{H}_2\text{O}$ and apparently $\text{Sr}(\text{ClO}_3)_2, 8\text{H}_2\text{O}$. Further, three modifications of the common anhydrous salt were obtained, differing from each other in crystalline form. It seems to me that the following fact throws most light on the nature of supersaturated solutions ; if crystals of two forms be simultaneously thrown into a supersaturated solution (for instance, of Na_2CO_3 , note 24) capable of depositing either of them, then only the less soluble form (solid phase) will crystallise out, whilst the more soluble form will pass into solution.

⁵⁷ **Emulsions**, such as milk, are composed of a solution of glutinous or similar substances, or of oily liquids suspended in a liquid in the form of drops, which are clearly visible under a microscope, and form an example of a mechanical formation resembling solution. But the difference from solutions is here evident. There are, however, solutions which approach very near to emulsions in the facility with which the dissolved substance separates from them. It has long been known, for example, that a particular kind of Prussian blue, $\text{KFe}_2(\text{CN})_6$, dissolves in pure water, but, on the addition of the smallest quantity of any one of a number of salts, it coagulates and becomes quite insoluble. If

Solutions of salts, on cooling below 0° , deposit ice or crystals (which frequently contain water of crystallisation) of the salt dissolved, and on reaching a certain degree of concentration they solidify in their entire mass. These solidified masses are termed *cryohydrates*. My researches on solutions of common salt (1868) showed that its solution solidifies when it reaches a composition $\text{NaCl} + 10\text{H}_2\text{O}$ (180 parts of water per 58.5 parts of salt), which takes place at about -23° . The solidified solution melts at the same temperature, and both the portion melted and the remainder preserve the above composition. Guthrie (1874–1876) prepared the cryohydrates of many salts, and he showed that certain of them are formed like the above at comparatively low temperatures, whilst others (for instance, those of corrosive sublimate, potassium chlorate and various colloids, and also the alums) are formed on a slight cooling—to -2° or even before.⁵⁸ In the case of common

copper sulphide (CuS), cadmium sulphide (CdS), arsenious sulphide (As_2S_3) (the experiments with these substances proceed with great ease, and the solution obtained is comparatively stable), or one of many other metallic sulphides be obtained by a method of double decomposition (by precipitating salts of these metals by hydrogen sulphide), and be then carefully washed (by allowing the precipitate to settle, pouring off the liquid, and again adding hydrogen sulphide solution), then, as was shown by Schulze, Spring, Prost, and others, the previously insoluble sulphides pass into transparent (for mercury, lead, and silver, reddish brown; for copper and iron, greenish brown; for cadmium and indium, yellow; and for zinc, colourless) solutions, which may be preserved (the weaker they are, the longer they keep), and even boiled, but which, nevertheless, in time coagulate—that is, separate in an insoluble form, and then sometimes become crystalline and quite incapable of redissolving. Graham and others observed the power shown by colloids (see note 18) of forming similar **hydrosols or solutions of gelatinous colloids**, and, in describing alumina and silica, we shall again have occasion to speak of such solutions.

In the existing state of our knowledge concerning solution, such solutions may be regarded as a transition between emulsions and ordinary solutions.

⁵⁸ Offer (1880) concludes, from his researches on cryohydrates, that they are simple mixtures of ice and salts, having a constant melting-point, just as there are alloys having a constant point of fusion, and solutions of liquids with a constant boiling-point (see note 60). This does not, however, explain in what form a salt is contained, for instance, in the cryohydrate $\text{NaCl} + 10\text{H}_2\text{O}$. At temperatures above -10° common salt separates out in anhydrous crystals, and at temperatures near -10° , in combination with water of crystallisation, as $\text{NaCl} + 2\text{H}_2\text{O}$; so that it is very improbable that at still lower temperatures it would separate without water. If the possibility of the solidified cryohydrate containing $\text{NaCl} + 2\text{H}_2\text{O}$ and ice be admitted, then it is not clear why one of these substances does not melt before the other. If alcohol extracts water from the solid mass leaving the salt behind, this does not prove the presence of ice, because alcohol also takes up water from the crystals of many hydrated substances (for instance, from $\text{NaCl} + 2\text{H}_2\text{O}$) at about their melting-points. Besides which, a simple observation on the cryohydrate, $\text{NaCl} + 10\text{H}_2\text{O}$, shows that with the most careful cooling it does not, on the addition of ice, deposit ice, if, as should be the case on solidification, ice were formed intermixed with the salt.

I may add with regard to cryohydrates, that many of the solutions of acids solidify completely on prolonged cooling (for example, $\text{H}_2\text{SO}_4, \text{H}_2\text{O}$), and then form perfectly definite compounds. From solutions of sulphuric acid (see Chapter XX.), for instance, Pickering obtained a hydrate, $\text{H}_2\text{SO}_4, 4\text{H}_2\text{O}$ at -25° . Hydrochloric, nitric, and other

salt the cryohydrate with 10 molecules of water, and in the case of sodium nitrate that ⁵⁹ with 7 molecules of water (i.e., 126 parts of water per 85 of salt), should be accepted as established substances, capable of passing from a solid to a liquid state, and conversely; and therefore *it may be thought* that in cryohydrates we have solutions which are not only undecomposable by cold, but also have a definite composition representing a fresh case of definite equilibrium between the solvent and the dissolved substance.

The formation of definite compounds in the process of solution becomes evident from the marked decrease of vapour pressure, or from the rise of the temperature of ebullition which occurs in the solution of certain volatile liquids and gases in water. As an example, we may take hydriodic acid, HI, a gas which liquefies, giving a liquid boiling at -34° . A solution of it containing 57 per cent. of hydriodic acid is distinguished by the fact that, if it is heated, the hydriodic acid and water volatilise together in the proportions in which they occur in the solution, so that such a solution may be distilled unchanged. The solution boils at a higher temperature than water, namely, at 127° . Some of the physical properties of the gas and water have in this case

acids also give similar crystalline hydrates, melting at low temperatures and presenting many similarities with the cryohydrates. It is my personal opinion that there exist the most varied and diverse stages of transition between molecular-physical and chemical reactions, and even between the mechanical juxtaposition of particles and their chemical interaction, and that cryohydrates (like solutions in general) form one of these stages. I therefore expect the most fruitful scientific results, not only from the application of physical conceptions to chemistry, but also from indications of the manifestation of chemical forces in the operations of molecular phenomena of a physico-mechanical order. This would bring about reconciliation between conceptions now in discord. To his researches on the heat evolved in the formation of the alloys of sodium and potassium, Joannis (1887) recognises the alloy NaK_2 as a definite compound (melting at -12.5°), as it is the most fusible and evolves the most heat. In 1901 N. S. Kurnakoff and N. A. Pushin showed in their researches on the melting-points that the alloy NaK_2 does indeed fuse at a lower temperature than all the other alloys of sodium and potassium, but came to the conclusion that this is only an instance of a cryohydrate or eutectic point and not of a definite compound, as in the case of cryohydrates (see Chap. XIII., note 21). The conception of the cryohydrate (in the case of solutions) or eutectic (in the case of alloys) point, according to the views of Le Chatelier and others, takes the following form. Imagine a solution or alloy of simple or compound substances A in B or conversely. The addition of B to A causes the melting-point of the latter to fall by an amount increasing with the amount of B added, although the melting-point of B may be higher than that of A, just as the temperature of formation of ice in solutions falls on the addition of a salt. But the same takes place on the addition of A to B (for instance, in alloys of tin and lead), only in the first instance A separates out in the solid state, and in the second B, which predominates. Evidently there must be some proportions of A and B, at which the decrements of the melting-points will coincide, and then the solidified alloy will contain both A and B. I cannot say for certain, but I think in general (there are probably different cases) that further study of this subject will elucidate certain aspects of the theory of solutions (see Chap. XVIII.)

⁵⁹ See note 24.

already disappeared—a new substance is formed, which has its definite boiling-point. To put it more correctly, this is not the temperature of ebullition, but the temperature at which the compound formed decomposes, yielding the vapours of the products of dissociation, which, on cooling, recombine. Should a less amount of hydriodic acid than the above be dissolved in water, then, on heating such a solution, water at first distils over alone, until the solution attains the above-mentioned composition; it will then distil over unaltered. If more hydriodic acid be passed into such a solution, a fresh quantity of the gas will dissolve, but it passes off with great ease, like air from water. It must not, however, be thought that those forces which determine the formation of ordinary gaseous solutions have no part whatever in the formation of a solution having a definite boiling-point; that they do come into play is shown by the fact that such constant gaseous solutions vary in their composition under different pressures.⁶⁰ It is not, therefore, at every, but only at the ordinary, atmospheric pressure that a constant boiling solution of hydriodic acid will contain 57 per cent. of the gas. At another pressure the proportions of water and hydriodic acid will be different. Judging, however, from observations made by Roscoe, the composition varies very little for considerable variations of pressure. This variation in composition indicates directly that pressure exerts an influence on the formation of unstable chemical compounds which are

⁶⁰ For this reason (the inconstancy of the composition of constant boiling solutions with a change of pressure), the existence of definite hydrates formed by volatile substances—for instance, by hydrochloric acid and water—is frequently denied. It is generally argued as follows: If there did exist a constancy of composition, then it would be unaltered by a change of pressure. But the distillation of constant boiling hydrates is undoubtedly accompanied (judging by the vapour densities determined by Bineau), like the distillation of sal-ammoniac, sulphuric acid, &c., by a complete decomposition of the original compound—that is, these substances do not exist in a state of vapour, but their products of decomposition (hydrochloric acid and water) are gases at the temperature of volatilisation and dissolve in the volatilised and condensed liquids; but the solubility of gases in liquids depends on the pressure, and therefore the composition of constant boiling solutions may, and even ought to, vary with a change of pressure; and, further, the smaller the pressure and the lower the temperature of volatilisation, the more likely is a true compound to be obtained. Sulphuric acid, H_2SO_4 , presents an instance of an undoubted chemical compound, and yet, as we shall see in Chap. XX., it gives off sulphuric anhydride on heating and decomposes when distilled. According to the researches of Roscoe and Dittmar (1859), the constant boiling solution of hydrochloric acid proved to contain 18 per cent. of hydrochloric acid at a pressure of 3 atmospheres, 20 per cent. at 1 atmosphere, and 23 per cent. at $\frac{1}{10}$ of an atmosphere. On passing air through the solution until its composition became constant (i.e., forcing the excess of aqueous vapour or of hydrochloric acid to pass away with the air) acid was obtained containing about 20 per cent. at 100° , about 23 per cent. at 50° , and about 25 per cent. at 0° . From this it is seen that either by decreasing the pressure or by lowering the temperature of evaporation one arrives at the same limit, where the composition must be taken as $\text{HCl} + 6\text{H}_2\text{O}$, which requires 25.26 per cent. of hydrochloric acid. Fuming hydrochloric acid contains more than this.

easily dissociated (with formation of a gas), just as it influences the solution of gases, the latter being, however, influenced to a greater degree than the former.⁶¹ Hydrochloric, nitric, and other acids form **solutions having definite boiling-points**, like that of hydriodic acid. They show, further, the common property, if containing but a small proportion of water, that they **fume in air**. Strong solutions of nitric, hydrochloric, hydriodic, and similar acids are even termed 'fuming acids.' The fuming liquids contain a definite compound whose temperature of ebullition (decomposition) is higher than 100° , and contain also an excess of the volatile substance dissolved, which exhibits a capacity to combine with water and form a hydrate the vapour pressure of which is less than that of aqueous vapour. On evaporating in air, this dissolved substance meets the atmospheric moisture and forms with it a visible vapour (fumes), consisting of the above-mentioned compound. The attraction or affinity which binds, for instance, hydriodic acid to water is evinced, not only in the evolution of heat and the diminution of vapour pressure (rise of boiling-point), but also in many purely chemical relations. Thus hydriodic acid is produced from iodine and hydrogen sulphide in the presence of water; but unless water is present this reaction does not take place.⁶²

Many **compounds containing water of crystallisation** are solid substances (when melted they are already solutions—i.e., liquids); furthermore, they are capable of being formed from solutions, like ice or aqueous vapour. They may be called **crystallo-hydrates**. Inasmuch as the direct presence of ice or aqueous vapour cannot be admitted in solutions, although the presence of water may be, so also there is no basis for acknowledging the presence in solutions of crystallo-hydrates, although they are obtained from solutions as such.⁶³ It is evident that

⁶¹ The essence of the matter may be thus represented. A gaseous or easily volatile substance, A , forms with a certain quantity of water, nH_2O , a definite complex compound, A, nH_2O , which is stable up to a temperature t° , higher than 100° . At this temperature it is decomposed into two substances, A and H_2O . Both boil below t° at the ordinary pressure, and therefore at t° they distil over and recombine in the receiver. But if a part of the substance A, nH_2O is decomposed or volatilised, there still remains in the vessel a portion of the undecomposed liquid which can partially dissolve one of the products of decomposition, and that in quantity varying with the pressure and temperature, so that the constant boiling-point solution will have a slightly different composition at different pressures.

⁶² For solutions of hydrochloric acid in water there are still greater differences in reaction. For instance, strong solutions decompose antimony sulphide (forming hydrogen sulphide, H_2S), and precipitate common salt from its solutions, whilst weak solutions do not act in this way.

⁶³ Supersaturated solutions give an excellent proof of this point. Thus a solution of copper sulphate generally crystallises in penta-hydrated crystals, $CuSO_4 + 5H_2O$, and a saturated solution gives such crystals when it is brought into contact with the minutest possible crystal of the same kind. But, according to the observations of Lecoq de

such substances present one of the many forms of equilibrium between water and a substance dissolved in it. This form, however, reminds one, in all respects, of solutions—that is, aqueous compounds which are more or less easily decomposed, with separation of water and the formation of a less aqueous or an anhydrous compound. In fact, there are not a few crystals containing water which lose a part of this water at the ordinary temperature. Such, for instance, are the crystals of soda, or sodium carbonate, which, when separated from an aqueous solution at the ordinary temperature, are quite transparent; but when left exposed to air, they lose a portion of their water, becoming opaque, and in the process lose their crystalline appearance, although preserving their original form. This process of the separation of water at the ordinary temperature is termed the **efflorescence** of crystals. Efflorescence takes place more rapidly under the receiver of an air-pump, and especially at a gentle heat. This breaking-up of a crystal is dissociation at the ordinary temperature. Solutions are decomposed in exactly the same manner.⁶⁴ The pressure of the aqueous vapour given off from crystallo-hydrates is naturally, as with solutions, less than the vapour pressure of water itself ⁶⁵ at the same temperature, and therefore many

Boisbaudran, if a crystal of ferrous sulphate (an isomorphous salt; see note 55), $\text{FeSO}_4 + 7\text{H}_2\text{O}$, be placed in a saturated solution of copper sulphate, then crystals of hepta-hydrated salt, $\text{CuSO}_4 + 7\text{H}_2\text{O}$, will be obtained. It is evident that neither the penta- nor the hepta-hydrated salt is contained as such in the solution. The solution presents its own particular liquid form of equilibrium (see note 24).

⁶⁴ Efflorescence, like evaporation, always proceeds from the surface. In the interior of crystals which have effloresced there is usually found a non-effloresced mass, so that the majority of effloresced crystals of washing soda show, in their fracture, a transparent nucleus coated by an effloresced, opaque, powdery mass. It is a remarkable circumstance that efflorescence proceeds in a perfectly regular and uniform manner, so that the angles and planes of similar crystallographic character effloresce simultaneously, and in this respect the crystalline form determines on which parts of crystals efflorescence starts, and the order in which it continues. In solutions, evaporation also proceeds from the surface, and the first crystals which appear when the required degree of saturation is reached are also formed at the surface. After falling to the bottom the crystals naturally continue to grow (see Chapter X., note 12).

⁶⁵ According to Lescœur (1883), at 100° a concentrated solution of barium hydroxide, BaH_2O_2 , on first depositing crystals (with $1\text{H}_2\text{O}$), has a pressure of about 630 mm. (instead of 760 mm., the pressure of water), which decreases (because the solution evaporates) to 45 mm., when all the water is expelled and only the crystals, $\text{BaH}_2\text{O}_2 + \text{H}_2\text{O}$ left; the latter then also lose water (dissociate, effloresce at 100°), leaving the hydroxide, BaH_2O_2 , which at 100° is perfectly undecomposable; that is, does not part with water. At 73° (the pressure of water is then 265 mm.) a solution containing $33\text{H}_2\text{O}$, on crystallising, has a pressure of 230 mm. and the crystals $\text{BaH}_2\text{O}_2 + 8\text{H}_2\text{O}$, which separate out, have a pressure of 160 mm., and on losing water give $\text{BaH}_2\text{O}_2 + \text{H}_2\text{O}$. This substance does not decompose at 73° , and therefore its pressure = 0. In those crystallo-hydrates which effloresce at the ordinary temperature, the pressure of dissociation approximates closely to that of the aqueous vapour, as was shown by Lescœur (1891). To this category of compounds belong $\text{B}_2\text{O}_3, (3+x)\text{H}_2\text{O}$; $\text{C}_2\text{O}_4\text{H}_2, (2+x)\text{H}_2\text{O}$; $\text{BaO}, (9+x)\text{H}_2\text{O}$, and $\text{SrO}, (9+x)\text{H}_2\text{O}$. And a still greater pressure is possessed

anhydrous salts which are capable of combining with water absorb aqueous vapour from moist air; that is, they act like a cold body, on which steam condenses. It is on this that the desiccation of gases is based, and it must further be remarked in this respect that certain substances—for instance, potassium carbonate (K_2CO_3) and calcium chloride ($CaCl_2$)—not only absorb the water necessary for the formation of a solid crystalline compound, but also give solutions, or **deliquesce**, as it is termed, in moist air. Many crystals do not effloresce in the least at the ordinary temperature; for example, copper sulphate, which may be preserved for an indefinite length of time without efflorescing (because its vapour pressure is less than that of the moisture in the air), but if it be placed under the receiver of an air-pump, and efflorescence be once started, it goes on at the ordinary temperature. The temperature at which the complete separation of water from crystals takes place varies considerably, not only for different substances, but also for different portions of the contained water of any one substance. Very often the temperature at which dissociation begins is very much higher than the boiling-point of water. Thus, for example, copper sulphate, which contains 36 per cent. of water, gives up 28·8 per cent. at 100° , and the remainder, namely, 7·2 per cent., only at 240° . Alum, out of the 45·5 per cent. of water which it contains, gives up 18·9 per cent. at 100° , a further 17·7 per cent. at 120° , 7·7 per cent. at 180° , and 1 per cent. at 280° ; it only loses the remainder (1 per cent.) at its temperature of decomposition. These examples clearly show that the taking-up of water of crystallisation is accompanied by a rather profound, although, in comparison with instances which we shall consider later, still inconsiderable, change of its properties. In certain cases the water of crystallisation is only given off when the solid form of the substance is destroyed, i.e., when the crystals melt on heating. The crystals are then said **to melt in their water of crystallisation**. Further, after the separation of the water, a solid substance remains behind, so that by further heating of the molten mass it acquires a solid form. This is seen most clearly in

by $Na_2SO_4 \cdot 10H_2O$; $Na_2CO_3 \cdot 10H_2O$, and $MgSO_4 \cdot (7+x)H_2O$. Müller-Erzbach (1884) determines the pressure (with reference to liquid water) by placing tubes of the same length containing water and the substances experimented with in a desiccator, the rate of loss of water giving the relative pressure. Thus, at the ordinary temperature, crystals of sodium phosphate, $Na_2HPO_4 \cdot 12H_2O$, present a pressure of 0·7 compared with that of water, until they lose $5H_2O$, then 0·4 until they lose $5H_2O$ more, and on losing the last portions of water the pressure falls to 0·04 compared with that of water. It is clear that the different molecules of water are held by unequal forces. Of the five molecules of water in copper sulphate the first two are comparatively easily separated, even at the ordinary temperature (but only after several days in a desiccator, according to Latchinoff); the next two are more difficultly separated, and the last equivalent is retained even at 100° . This is another indication of the capacity of $CuSO_4$ to form three hydrates, $CuSO_4 \cdot 5H_2O$, $CuSO_4 \cdot 3H_2O$, and $CuSO_4 \cdot H_2O$. The

crystals of sugar of lead or lead acetate, which melt in their water of crystallisation at a temperature of 56.25° , and in so doing begin to lose water. On reaching a temperature of 100° the sugar of lead solidifies, having lost all its water; and then, at a temperature of 280° , the anhydrous and solidified salt again melts.^{65a}

It is most important to recognise, in respect to the water of crystallisation, that its ratio to the quantity of the substance with which it is combined is always constant. However often we may prepare copper sulphate, we shall always find 36.07 per cent. of water in its crystals, and these crystals always lose four-fifths of their water at 100° , while one-fifth of the whole amount of the contained water remains in the crystals at 100° , and is only expelled from them at a temperature of about 240° . What has been said about copper sulphate crystals applies also to all other crystals containing water of crystallisation. It is impossible in any of these cases to increase the relative proportion either of the salt or of the water without changing the homogeneity of the substance. If once a portion of the water is lost—for instance, if once efflorescence takes place—there is obtained not a homogeneous substance, but a mixture consisting of a substance deprived of water and one which has not yet lost water, i.e., decomposition has already commenced. This constant ratio is an example of the fact that in chemical compounds the proportions of the component parts are quite definite; that is, it is an example of the so-called **definite chemical compounds**. These may be distinguished from solutions, and from all other so-called indefinite chemical compounds, in that at least one, and sometimes both, of the component parts may be added in large quantity to an indefinite chemical compound without destroying the homogeneity, as in the case of solutions; whilst it is impossible to add to a definite chemical compound any one of its component parts without destroying the homogeneity of the entire mass. Definite chemical compounds only decompose on a certain rise in temperature; on lowering the temperature they do not, at least in but few cases, yield their components, as do solutions, which form ice or compounds containing water

researches of Andreae on the pressure of dissociation of hydrated copper sulphate showed (1891) the existence of three regions, characterised at a given temperature by constant pressures: (1) between 3 and 5, (2) between 1 and 3, and lastly (3) between 0 and 1 molecule of water, again confirming the existence of three hydrates of this salt having the above compositions.

^{65a} Sodium acetate ($\text{C}_2\text{H}_3\text{O}_2\text{Na}, 3\text{H}_2\text{O}$) melts at 58° , but resolidifies only on contact with a crystal, otherwise it may remain liquid even at 0° , and may be used for obtaining a constant temperature. According to Jeannel, the latent heat of fusion is about 28 calories, and according to Pickering the heat of solution is 35 calories. When melted, this salt boils at 123° , that is, the pressure of the vapour given off at that temperature equals the atmospheric pressure.

of crystallisation. This leads to the assumption that solutions contain water as water,⁶⁶ although it may sometimes be in very small quantity. So that solutions which are capable of solidifying completely (for instance, crystallo-hydrates capable of melting), such as the compound of $84\frac{1}{2}$ parts of sulphuric acid, H_2SO_4 , with $15\frac{1}{2}$ parts of water, H_2O , or $\text{H}_2\text{SO}_4\cdot\text{H}_2\text{O}$ (or H_4SO_5), appear as true definite chemical compounds. If, then, we imagine such a definite compound in a liquid state, and admit that in this state it partially decomposes, with the separation of water—not as ice or vapour (for then the system would be heterogeneous, containing substances in different physical states), but in a liquid form, when the system will be homogeneous—we shall form an idea of a solution as an unstable, dissociating fluid state of equilibrium between water and the substance dissolved.^{66a} Moreover, it should be remarked that, judging by experiment, many substances give with water not one but several *different* compounds,⁶⁷ as is seen in the capacity of one substance to form with water many different **crystallo-hydrates**, or compounds with water of crystallisation, showing diverse and independent

⁶⁶ Such a phenomenon frequently presents itself in purely chemical actions. For instance, let a liquid substance *A* give, with another liquid substance *B*, under certain experimental conditions, only a minute quantity of a solid or gaseous substance *C*. This small quantity will separate out (pass away from the sphere of action, as Berthollet expressed it), and the remaining masses of *A* and *B* will again give *C*; consequently under these conditions action will go on to the end. Such, it seems to me, is the action in solutions when they yield ice or vapour indicating the presence of water.

^{66a} A difficulty in understanding solutions is here met with in the fact that it is necessary to admit the interpenetration (entire uniform intermixture) of two liquids, water and the liquid compound. But if gases and vapours of all kinds intermix in all proportions by virtue of the mobility of their particles, of their elasticity, and of the radical similarity of their structure, there is no reason why these properties should be denied to liquids, as much in them is akin to gases; and if liquids resemble each other, the intermixture or interpenetration of their particles is also admissible, more especially as particles of different substances are found mixed together in the crystals of similar (isomorphous) substances.

⁶⁷ Certain substances on combining are capable of forming together only one compound, whilst others yield several, and these of the most varied degrees of stability. The compounds of water are instances of this kind. In solutions the existence of several different definite compounds must be acknowledged, but many of these have not yet been obtained in a free state, and it may be that they cannot be obtained in any other than a liquid form—that is, dissolved—just as there are many undoubted definite compounds which only exist in one physical state. Such instances occur among the hydrates. The compound $\text{CO}_2 + 8\text{H}_2\text{O}$ (see note 31), according to Wroblewski, only occurs in a solid form. Hydrates like $\text{H}_2\text{S} + 12\text{H}_2\text{O}$ (De Forcrand and Villard), $\text{HBr} + \text{H}_2\text{O}$ (Roozeboom), are recognised only by a decrease of pressure and are very transient substances, incapable of stable existence in a free state. Even sulphuric acid, H_2SO_4 , itself, which is undoubtedly a definite compound, fumes in a liquid form, giving off the anhydride, SO_3 , and this exhibits a very unstable equilibrium. The crystallo-hydrates of chlorine, $\text{Cl}_2 + 8\text{H}_2\text{O}$, of hydrogen sulphide, $\text{H}_2\text{S} + 12\text{H}_2\text{O}$ (formed at 0° , and completely decomposed at $+1^\circ$, when 1 vol. of water only dissolves 4 vols. of hydrogen sulphide, while at 0.1° it dissolves about 100 vols.), and of many other gases, are instances of hydrates which are very unstable.

properties. From these considerations, *solutions* ⁶⁸ *may be regarded as definite, unstable liquid chemical compounds in a state of dissociation.* ⁶⁹

Regarding solutions from this point of view, they come under the head of those definite compounds with which chemistry is mainly concerned. ⁷⁰

⁶⁸ Of such a kind are also other indefinite chemical compounds, for example, metallic alloys. These are solid substances or solidified solutions of metals. They also contain definite compounds, and may contain an excess of one of the metals. According to the experiments of Laurie (1888), the alloys of zinc with copper behave, in respect to their electromotive force in galvanic batteries, just like zinc, if the proportion of zinc does not exceed a certain percentage—that is, so long as a definite compound is not formed—for in that case particles of free zinc are present; but if a copper plate be taken, and only one-thousandth part of its area be covered by zinc, then the zinc alone will act in a galvanic battery.

⁶⁹ According to the above supposition, the condition of solutions in the sense of the kinetic hypothesis of matter (that is, on the supposition of an internal motion of molecules and atoms) may be represented in the following form:—In a homogeneous liquid—for instance, water—the molecules occur in a certain state of equilibrium, which, although mobile, is stable. When a substance A dissolves in water, its molecules form, with several molecules of water, systems, A, nH_2O , which are so unstable that when surrounded by molecules of water they decompose and re-form, so that A passes from one group of water molecules to another, and the molecules of water which were at one moment in harmonious motion with A in the form of the system A, nH_2O , in the next instant may have already succeeded in getting free. The addition of water or of molecules of A may either only alter the number of free molecules, which in their turn enter into systems A, nH_2O , or it may introduce conditions for the possibility of building up new systems A, mH_2O , where m is either greater or less than n . If the relation of the molecules in the solution were the same as in the system A, mH_2O , then the addition of fresh molecules of water or of A would be followed by the formation of new molecules A, nH_2O . The relative quantity, stability, and composition of these systems or definite compounds will vary in one or another solution. I adopted this view of solutions in 1887 (Pickering subsequently putting forward a similar view) after a most intimate study of the variation of their specific gravities, to which my book, cited in note 19, is devoted. Substances A , which give solutions, are distinguished by the fact that they can form such unstable systems, A, nH_2O , but besides these they may give other much more stable systems, A, n_1H_2O . Thus ethylene, C_2H_4 , in dissolving in water probably forms a system, C_2H_4, nH_2O , which easily splits up into C_2H_4 and H_2O , but it gives also the system alcohol, C_2H_4, H_2O or C_2H_6O , which is comparatively stable. Further, oxygen can dissolve in water, and it can also combine with it, forming peroxide of hydrogen. Turpentine, $C_{10}H_{16}$, does not dissolve in water, but it combines with it, giving a comparatively stable hydrate. In other words, the chemical structure of hydrates or of the definite compounds contained in solutions, is distinguished, not only by its peculiar characters, but also by a diversity of stability.

⁷⁰ The above representation of solutions and other indefinite compounds, considering them as a particular state of definite compounds, excludes the independent existence of indefinite compounds; in this way, that unity of chemical conception is obtained which cannot be arrived at by admitting the physico-mechanical conception of indefinite compounds. The gradual transition from typical solutions (such as those of gases in water and weak saline solutions) to sulphuric acid, and from it and its definite but yet unstable and liquid compounds, to clearly defined compounds, such as salts and their crystallo-hydrates, is so imperceptible that in denying that solutions belong to the number of definite but dissociating compounds we risk denying the definiteness of the atomic composition of such substances as sulphuric acid or molten crystallo-hydrates. I repeat, however, that

We saw above that copper sulphate loses four-fifths of its water at 100° and the remainder at 240° . This means that there are two definite compounds of water with the anhydrous salt. Washing soda or carbonate of sodium, Na_2CO_3 , separates out from its solutions at the ordinary temperature as crystals, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, containing 62.9 per cent. of water by weight. When a solution of the same salt deposits crystals at a low temperature, about -20° , these crystals contain 71.8 parts of water to 28.2 of the anhydrous salt. Further, the crystals are obtained together with ice, and are left behind when the latter melts. If ordinary soda, with 62.9 per cent. of water, be cautiously melted in its own water of crystallisation, there remains a salt, in a solid state, containing only 14.5 per cent. of water, and a liquid is obtained which at 34° deposits crystals which contain 46 per cent. of water and do not effloresce in the air. Lastly, if a supersaturated solution of soda be prepared at temperatures below 8° , it deposits crystals containing 54.3 per cent. of water. Hence as many as five compounds of anhydrous soda with water are known, and they are dissimilar in their properties and crystalline forms, and even in their solubilities. There is apparently no relation between the above quantities of water and salt, but this is only because in each case the amounts of water and anhydrous salt were given in percentages; if the amounts of water be calculated for one and the same quantity of anhydrous salt, great regularity will be observed in the proportions of the component parts in all these compounds. It appears that for 106 parts of anhydrous salt there are, in the crystals separated out at -20° , 270 parts of water; in the crystals obtained at 15° , 180 parts of water; in those obtained from a supersaturated solution, 126 parts; in the crystals which separate out at 34° , 90 parts; and in the crystals with the smallest amount of water, 18 parts. On comparing these quantities of water it will readily be seen that they are very simply related to each other, for they are all divisible by 18, and are in the ratio 15 : 10 : 7 : 5 : 1. Naturally, direct experiment, however carefully it be conducted, is hampered with errors; but taking these unavoidable experimental errors into consideration, it will be seen that for a given quantity of the anhydrous salt there occur, in its various compounds with water, quantities of water which are in very simple multiple proportion. This is observed in, for the present the theory of solutions cannot be considered as firmly established. The above opinion concerning them is nothing more than an hypothesis. By submitting solutions to the Daltonic conception of atomism, I hope that we may not only attain to a general harmonious chemical doctrine, but also that new motives for investigation and research will appear in the problem of solutions, which must either confirm the proposed theory or replace it by another, fuller and truer; and I, for my part, cannot consider this to be the case with any of the other present doctrines of solutions (note 49).

and is common to, all definite chemical compounds. This rule is called **the law of multiple proportions**. It was discovered by Dalton, and will be evolved in further detail subsequently in this work. For the present we will only state that the law of definite composition enables the composition of substances to be expressed by formulæ, and the law of multiple proportions permits the application of whole numbers as coefficients of the symbols of the elements in these formulæ. Thus the formula $\text{Na}_2\text{CO}_3, 10\text{H}_2\text{O}$ shows directly that in this crystallo-hydrate there are 180 parts of water to 106 parts by weight of the anhydrous salt, because the formula of soda, Na_2CO_3 , corresponds with a weight of 106, and the formula of water to 18 parts by weight, which are here taken ten times.

In the above examples of the combinations of water, we saw the gradually increasing intensity of the bond between water and a substance with which it forms a homogeneous compound. There is a series of such compounds with water, in which the latter is held with very great force, and is only given up at a very high temperature, and indeed, in some cases, cannot be separated by any degree of heat without completely decomposing the substance. In these compounds there is generally no outward sign whatever that they contain water. A perfectly new substance is formed from an anhydrous substance and water, in which sometimes the properties of neither one nor the other component are observable. In the majority of cases a considerable amount of heat is evolved in the formation of such compounds with water. Sometimes this evolution is so intense that a red heat is produced and light emitted. After this it is hardly to be wondered at that stable compounds are formed by such combinations. Their decomposition requires much heat; a large amount of work is necessary to separate them into their component parts. All such compounds are definite, and, as a rule, quite distinctly definite. Such definite compounds with water are called **hydrates**. The water contained in these compounds is often called **water of constitution**, i.e., water which enters into the structure or composition of the given substance. By this it is desired to express that in other cases the molecules of water are, as it were, separate from the molecules of the substance with which it is combined. It is supposed that, in the formation of hydrates, this water, even in the smallest particles, forms one complete whole with the anhydrous substance. Many examples of the formation of such hydrates might be cited. The most familiar example in practice is the hydrate of lime, or so-called 'slaked' lime. Lime is prepared by burning limestone, by which the carbonic anhydride is expelled from it and there remains a white stony mass, which is dense, compact, and somewhat tenacious. Lime is

usually sold in this form, which bears the name of 'quick' or 'unslaked' lime. If water be poured over such lime, a considerable rise in temperature is remarked either directly or after a certain time. The whole mass becomes hot, part of the water is evaporated, the stony mass in absorbing water crumbles into powder, and if the water be taken in sufficient quantity, and the lime be pure and well burnt, not a particle of the original stony mass is left—it all crumbles into powder. If the water be in excess, then naturally a portion of it remains and forms a solution. This process is called 'slaking' lime. Slaked lime is used in practice mixed with sand as mortar. Slaked lime is a definite hydrate of lime. If it is dried at 100° , it retains 24.3 per cent. of water. This water can only be expelled at a temperature above 400° , and then quicklime is obtained again. The heat evolved in the combination of lime with water is so intense that it can set fire to wood, sulphur, gunpowder, &c. Even on mixing lime with ice, the temperature rises to 100° . If lime is moistened with a small quantity of water in the dark, a luminous effect is observed. The reaction which takes place is as follows: $\text{CaO} + \text{H}_2\text{O} = \text{CaH}_2\text{O}_2$. But, nevertheless, water may still be separated from this hydrate.⁷¹ If phosphorus be burnt in dry air, a white substance called 'phosphoric anhydride' is obtained. This combines with water with such energy that the experiment must be conducted with great caution. A red heat is produced in the formation of the compound, and it is impossible to separate the water from the resultant hydrate at any temperature. The hydrate formed by phosphoric anhydride is a substance which is totally undecomposable into its original component parts by the action of heat. Almost as energetic a combination occurs when sulphuric anhydride, SO_3 , combines with water, forming its hydrate, sulphuric acid, H_2SO_4 . In both cases definite compounds are produced, but the latter substance, as a liquid, and capable of decomposition by heat, forms an evident link with solutions. If 80 parts of sulphuric anhydride combine with 18 parts of water, this water cannot be separated from the anhydride, even at a temperature of 300° . It is only by the addition of phosphoric anhydride, or by a series of chemical transformations, that water can be separated from its combination with sulphuric anhydride. This compound is oil of vitriol, or sulphuric acid. If a larger proportion of water be taken, it will combine with the H_2SO_4 ; for instance, if 36

⁷¹ In combining with water, one part by weight of lime evolves 245 units of heat. A high temperature is obtained, because the specific heat of the resulting product is small. Sodium oxide, Na_2O , in reacting on water, H_2O , and forming caustic soda (sodium hydroxide), NaHO , evolves 552 units of heat for each part by weight of sodium oxide, and the resulting hydrate decomposes entirely on ignition, without the separation of water.

parts of water per 80 parts of sulphuric anhydride be taken, a compound is formed which crystallises in the cold, and melts at $+8^{\circ}$, whilst oil of vitriol does not solidify even at -30° . If still more water be taken, the oil of vitriol will dissolve in the remaining quantity of water. An evolution of heat takes place, not only on the addition of the water of constitution, but in a less degree on further additions of water;⁷² and therefore there is no distinct boundary, but only a gradual transition, between those chemical phenomena which are expressed in the formation of solutions and those which take place in the formation of the most stable hydrates.⁷³

⁷² The diagram given in note 28 shows the evolution of heat on mixing sulphuric acid, or the mono-hydrate (H_2SO_4 , i.e., $\text{SO}_3 + \text{H}_2\text{O}$), with different quantities of water per 100 vols. of the resultant solution. Every 98 grams of sulphuric acid (H_2SO_4) evolve, on the addition of 18 grams of water, 6,379 units of heat; with twice or three times the quantity of water 9,418 and 11,137 units of heat, and with an infinitely large quantity of water 17,860 units of heat, according to the determinations of Thomsen. The latter also showed that when H_2SO_4 is formed from SO_3 (=80) and H_2O (=18), 21,308 units of heat are evolved for every 98 parts by weight of the resultant sulphuric acid.

⁷³ Thus for different hydrates the stability with which the water is held is very dissimilar. Certain hydrates hold water very loosely, and in combining with it evolve little heat. From other hydrates the water cannot be separated by any degree of heat, even if they are formed from anhydrides (i.e., anhydrous substances) and water with but little evolution of heat; for instance, acetic anhydride in combining with water evolves an inconsiderable amount of heat, but the water cannot afterwards be expelled. If the hydrate (acetic acid) formed by this combination be strongly heated, it either volatilises without change, or decomposes into new substances, but it does not again yield the original substances, namely, the anhydride and water, at least in a liquid form. Here is an instance which gives the reason for calling the water entering into the composition of the hydrate 'water of constitution.' Such, for example, is the water entering into the so-called caustic soda or sodium hydroxide (see note 71). But there are hydrates which easily part with their water; yet this water cannot be considered as water of crystallisation, not only because sometimes such hydrates have no crystalline form, but also because in perfectly analogous cases very stable hydrates are formed, capable of particular kinds of chemical reactions, as we shall subsequently learn. Such, for example, is the unstable hydrated oxide of copper, which is not formed from water and oxide of copper, but which is obtained just like far more stable hydrates, for example, the hydrated oxide of barium, BaH_2O_2 , or $\text{BaO} + \text{H}_2\text{O}$, by the double decomposition of the solution of salts with alkalies. In a word, there is no distinct boundary either between the water of hydrates and of crystallisation, or between solution and hydration.

It must be observed that, in separating from an aqueous solution, many substances, without having a crystalline form, hold water in the same unstable state as in crystals; but this water cannot be termed 'water of crystallisation' if the substance which separates out has no crystalline form. The hydrates of alumina and silica are examples of such unstable hydrates. If these substances are separated from an aqueous solution by a chemical process, they always contain water. The formation of a new chemical compound containing water is here particularly evident, for alumina and silica in an anhydrous state have chemical properties differing from those they show when combined with water, and do not combine directly with it. The entire series of colloids on separating from water form with it similar compounds, which have the aspect of solid gelatinous substances. Water is held in considerable quantity in solidified glue or boiled albumin. It cannot be expelled from them by pressure; hence in this case there has ensued some kind of combination of the substance with water. This water is, however, easily separated

We have thus considered many aspects and degrees of combination of various substances with water, or instances of the **compounds of water**, when it and other substances form new homogeneous substances, which in this case will evidently be complex, i.e., made up of different substances; and although they are homogeneous, yet it must be admitted that there exist in them those component parts which entered into their composition, inasmuch as these parts may be again obtained from them. It must not be imagined that water really exists in hydrate of lime, any more than that ice or steam exists in water. When we say that water occurs in the composition of a certain hydrate, we only wish to point out that there are chemical transformations in which it is possible to obtain that hydrate by means of water, and other transformations in which this water may be separated out from the hydrate. This is all simply expressed by saying that water enters *into the composition* of this hydrate. And the study of the composition of compounds, that is, the expression of their transformations, forms one of the chief problems of chemistry, when our study is limited to the elements, or simple substances.

on drying; but not the whole of it, as a portion is retained, and this portion is considered to belong to the hydrate, although in this case it is very difficult, if not impossible, to obtain definite compounds. The absence of any distinct boundary lines between solutions, crystallo-hydrates, and ordinary hydrates above referred to is very clearly seen in such examples.

CHAPTER II

THE COMPOSITION OF WATER ; HYDROGEN

THE question now arises, Is not **water** itself a **compound substance**? Can it not be formed by the mutual reaction of some component parts? Can it not be broken up into its component parts? There cannot be the least doubt that if it does split up, and if it is a compound, then it is a **definite** one characterised by the stability of the union between those component parts from which it is formed. From the fact alone that water passes into all physical states as a homogeneous whole, without in the least varying chemically in its properties and without splitting up into its component parts (neither solutions nor many hydrates can be distilled—they are split up), we must conclude, that if water is a compound, then it is a stable and definite chemical compound capable of entering as a whole into many other combinations. As with all other great discoveries in the province of chemistry, it is to the end of the eighteenth century that we are indebted for the important discovery that water is not a simple substance, but that, like a number of other compound substances, it is composed of two separate substances. This was proved by two of the methods by which the compound nature of bodies may be directly determined: by analysis and by synthesis, that is, by the decomposition of water into, and by the formation of water from, its component parts. In 1781 Cavendish first obtained water by burning hydrogen in oxygen, both of which gases were already known to him. He concluded from this that water was composed of two substances. But he did not make more accurate experiments, which would have shown the relative quantities of the component parts in water, and which would have determined its complex nature with certainty. Although his experiments were the first, and although the conclusion he drew from them was a true one, yet such novel ideas as the complex nature of water are not easily recognised so long as there is no series of researches which completely and indubitably proves the truth of such conclusions. The fundamental experiments which really proved the complexity of water by the method

of synthesis, and its formation from other substances, were made in 1789 by Monge, Lavoisier, Fourcroy, and Vauquelin. They obtained four ounces of water by burning hydrogen, and found that 100 parts of water contain 15 parts of hydrogen and 85 parts of oxygen. It was also proved that the weight of water formed was equal to the sum of the weights of the component parts entering into its composition; consequently water contains all the matter entering into oxygen and hydrogen, and no other. The compound nature of water was proved in this manner by a method of synthesis. But we will turn to its analysis, i.e., to its decomposition into its component parts. The analysis may be more or less complete. Either both component parts may be obtained in a separate state, or else only one is separated and the other converted into a new compound in which its amount may be determined by weighing. This will be a reaction of substitution such as is often taken advantage of in analysis. The first analysis of water was conducted in this way by Lavoisier and Meusnier in 1784. The apparatus they employed consisted of a glass retort containing water previously purified, of which the weight had been determined. The neck of the retort was inserted into a porcelain tube, placed inside an oven, and heated to a red heat by means of charcoal. Iron filings, which decompose water at a red heat, were placed inside this tube, the end of which was connected with a worm, for the purpose of condensing any water which might pass through the tube undecomposed. This condensed water was collected in a separate flask. The gas formed by the decomposition was collected over water in a bell jar. The aqueous vapour in passing over the red-hot iron was decomposed, and a gas was formed from it whose weight could be determined from its volume and its known density. Besides the water which passed through the tube unaltered a certain quantity of water disappeared in the experiment, and this quantity, in the experiments of Lavoisier and Meusnier, was equal to the weight of gas collected in the bell jar plus the increase in weight of the iron filings. Hence the water was decomposed into a gas, which was collected in the bell jar, and a substance, which combined with the iron, and is consequently composed of these two component parts. This was the first analysis of water ever made; but here only one (and not both) of the gaseous components of water was collected separately. Both the component parts of water can, however, be simultaneously obtained in a free state. For this purpose the decomposition is brought about by a galvanic current or by heat, as we shall learn directly.¹

¹ The first experiments on the synthesis and decomposition of water did not afford, however, an entirely convincing proof that water was composed of hydrogen and oxygen

Water is a bad conductor of electricity, that is, pure water is incapable of transmitting a feeble current; but if any salt or acid be dissolved in it, its conductivity increases, and **on the passage of a current** through acidified water **it is decomposed** into its component parts. A little sulphuric acid is generally added to the water. By immersing platinum plates (electrodes) in this water (platinum is chosen because it is not attacked by acids, which act chemically on many other metals) and connecting them with a galvanic battery it will be observed that bubbles of gas appear on these plates. The gas which separates is called **detonating gas**,² because on ignition it very readily explodes.³ What takes place is as follows. The water, by the action of the current, is decomposed into two gases. The mixture of these gases forms detonating gas, and when this is brought into contact with an incandescent substance—for instance, a lighted taper—the gases recombine, forming water, the combination being accompanied by a great evolution of heat, so that the vapour of the water formed expands considerably and very rapidly, and as a consequence an explosion takes place—that is, sound and increase of pressure, and atmospheric disturbance, as in the explosion of gunpowder.

In order to discover what gases are obtained by the decomposition of water, the gases which are given off at the two electrodes must be collected separately. For this purpose a V-shaped tube is taken, one end being open and the other fused up. A platinum wire, terminating inside the tube in a plate, is fused into the closed end, which is entirely

alone. Davy, who investigated the decomposition of water by the galvanic current, thought for a long time that, besides these gases, an acid and alkali were also obtained. He was only convinced of the fact that water contains nothing but hydrogen and oxygen by a long series of researches, which showed him that the appearance of an acid and alkali in the decomposition of water proceeds from the presence of impurities (especially ammonium nitrate) in the water. A final comprehension of the composition of water is obtained from the accurate determination of the quantities of the component parts which enter into its composition. It will be seen from this how many data are necessary for proving the composition of a substance—that is, of the transformations of which it is capable. What has been said of water refers to all other compounds; the investigation of each one, the entire proof of its composition, can only be obtained by the accumulation of a large mass of data referring to it.

² This gas is collected in a voltameter.

³ In order to observe this explosion without the slightest danger, it is best to proceed in the following manner. Some soapy water which easily forms soap bubbles is prepared and poured into an iron trough. In this water the end of a gas-conducting tube is immersed. This tube is connected with any suitable apparatus in which detonating gas is evolved. In this way soap bubbles full of this gas are formed. If the apparatus in which the gas is produced be then removed (otherwise the explosion might travel into the interior of the apparatus), and a lighted taper be brought to the soap bubbles, a very sharp explosion will take place. The bubbles should be small to avoid any danger; ten, each about the size of a pea, suffice to give a sharp report like a pistol-shot.

filled with water⁴ acidified with sulphuric acid, and another platinum wire, terminating in a plate, is immersed in the open end. If a current from a galvanic battery be now passed through the wires, an evolution of gases will be observed, that obtained in the open branch passing into the air, while that in the closed branch accumulates above the water. As this latter gas accumulates it displaces the water, which continues to descend in the closed and ascend in the open branch of the tube. When the water in this way reaches the top of the open end, the passage of the current is stopped, and the gas evolved from one of the electrodes only is obtained in the apparatus. By this means it is easy to prove that a distinct gas appears at each electrode. If the closed end be the cathode, i.e., be connected with the negative pole of the battery (the zinc), then the gas collected in the apparatus is capable of

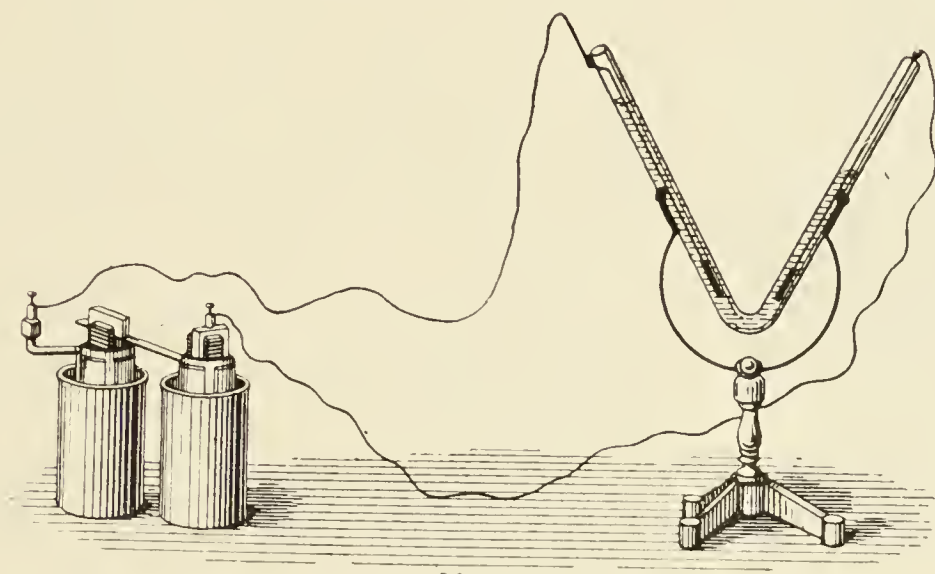


FIG. 18.—Decomposition of water by the galvanic current.

burning. This may be demonstrated by the following experiment. The bent tube is taken from the stand, its open end stopped up with the thumb and the tube inclined in such a manner that the gas passes from the closed into the open end. It will then be found, on applying a lighted lamp or taper, that the gas burns. This combustible gas, which collects at the cathode or negative electrode, is **hydrogen**. If the same experiment be carried on with a current passing in the opposite direction—that is, if the closed end be joined up with the positive pole, (i.e., with the carbon, copper, or platinum)—then the gas which is evolved from it does not itself burn, but it supports combustion very vigorously, so that a smouldering taper placed in it immediately bursts into flame. This gas, which is collected at the anode or positive pole, is

⁴ In order to fill the tube with water it is turned up, so that the closed end points downwards and the open end upwards, water acidified with sulphuric acid being then poured into it.

oxygen, which is obtained, as we saw before (in the Introduction,, from mercury oxide, and is contained in air.

Thus, in the decomposition of water, oxygen appears at the positive pole and hydrogen at the negative pole ^{4a}; so that detonating gas will be a mixture of both. Hydrogen burns in air from the fact that in doing so it forms water with the oxygen of the air. Detonating gas explodes owing to the hydrogen burning in the oxygen mixed with it. It is very easy to measure the relative quantities of one and the other

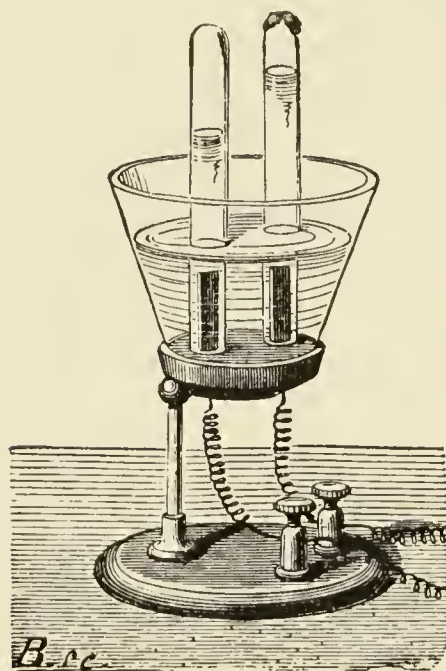


FIG. 19.—Decomposition of water by the galvanic current, for determining the relation between the volumes of hydrogen and oxygen.

gas which are evolved in the decomposition of water. For this purpose a funnel is taken whose orifice is closed by a cork through which pass two platinum wires connected with a battery. Acidified water is poured into the funnel and a glass cylinder full of water is placed over the end of each wire (fig. 19). On passing a current, hydrogen and oxygen collect in these cylinders, and it will easily be seen that two volumes of hydrogen are evolved for every one volume of oxygen. This signifies that in decomposing, water gives two volumes of hydrogen and one volume of oxygen.

Water is also decomposed into its component parts by **the action of heat**. At the melting-point of silver (950°), and in its presence, water is decomposed and the oxygen absorbed by the molten silver, which dissolves it so long as it is liquid. But directly the silver solidifies the oxygen is expelled from it. This experiment is, however, not entirely convincing; it might be thought that in this case the

^{4a} Owing to the gradual but steady progress made during the last quarter of the nineteenth century in the production of an electric current from the dynamo and its transmission over considerable distances, the electrolytic decomposition of many compound bodies has acquired great importance, and the use of the electric current is making its way into many chemical manufactures. Hence Prof. D. A. Lachinoff's proposal to obtain hydrogen and oxygen (both of which have many applications) by means of electrolysis (of either a 10 to 15 per cent. solution of caustic soda or a 15 per cent. solution of sulphuric acid) may find a practical application, at all events at some future time. Owing to their simplicity, electrolytic methods of decomposition have a great future; but as yet, so long as the production of an electric current remains so costly, their application is limited. And for this reason, although certain of these methods are mentioned in this work, they are not specially considered, the more so since a profitable and proper use of the electric current for chemical purposes requires special electro-technical knowledge which beginners cannot be assumed to have, and therefore an exposition of the principles of electro-technology as applied to the production of chemical transformations, although referred to in places, does not come within the scope of the present work.

decomposition of the water did not proceed from the action of heat, but from the action of the silver on water—that silver decomposes water, taking up the oxygen. If steam be passed through a red-hot tube, the interior of which is at a temperature of $1,000^{\circ}$, a portion⁵ of the water decomposes into its component parts, forming detonating gas. But on passing into the cooler portions of the apparatus this detonating gas again forms water, since the hydrogen and oxygen obtained combine at a lower temperature.⁶ The problem of showing the decomposability of water at high temperatures is apparently unsolvable. It was considered as such before Henri Sainte-Claire Deville (in the fifties) introduced into chemistry the conception of dissociation; that is, a change of chemical state resembling evaporation (if decomposition be likened to boiling), and before he had demonstrated the decomposability of water by the action of heat in an experiment which will presently be described. In order to demonstrate clearly the **dissociation** of water, or its decomposability by heat, at a temperature approaching that at which it is formed, it was necessary to separate the hydrogen from the oxygen at a high temperature without allowing

⁵ As water is formed by the combination of oxygen and hydrogen, with a considerable evolution of heat, and as it can also be decomposed, this reaction is a reversible one (see Introduction), and consequently at a high temperature the decomposition of water cannot be complete—it is limited by the opposite reaction. Strictly speaking, it is not known how much water is decomposed at a given temperature, although many efforts (by Bunsen and others) have been made in various directions to solve this question. Our small knowledge of the coefficient of expansion, and of the specific heat of gases at such high temperatures, renders all calculations (from observations of the pressure on explosion) of doubtful value.

⁶ Grove, in 1847, observed that a platinum wire fused in the oxy-hydrogen flame—that is, having acquired the temperature of the formation of water—forms at its end a molten drop which in falling into water evolves detonating gas, that is, decomposes the water. It therefore follows that water decomposes at the temperature of its formation. At that time this formed a scientific paradox, which we shall unravel only with the development of the conceptions of dissociation, introduced into science by Henri Sainte-Claire Deville in 1857. These conceptions form an important epoch in science, and their development is one of the problems of modern chemistry. The essence of the matter is that, at high temperatures, water exists, but also decomposes, just as a volatile liquid, at a certain temperature, exists both as a liquid and as a vapour. Similarly as a volatile liquid saturates a space, attaining its maximum pressure, so also the products of dissociation have their maximum pressure; and when once that is attained decomposition ceases, just as evaporation does. Under like conditions, if the vapour be allowed to escape (and therefore its partial pressure be diminished) evaporation will recommence; so also if the products of decomposition be removed decomposition again proceeds. These simple conceptions of dissociation introduce infinitely varied consequences into the mechanism of chemical reactions, and we shall therefore have occasion to return to them very often. We may add that Grove also concluded that water is decomposed at a white heat from the fact that he obtained detonating gas by passing steam through a tube containing a wire heated strongly by an electric current, and that by passing steam over molten oxide of lead he obtained, on the one hand, minium (= oxide of lead plus oxygen), and, on the other, metallic lead, formed by the action of the hydrogen

the mixture to cool. To do this, Deville took advantage of the difference between the densities of hydrogen and oxygen.

A wide porcelain tube *p* (fig. 20) is placed in a furnace, which can be raised to a high temperature (it should be heated with small pieces of good coke). In this tube there is inserted a second tube, *t*, of smaller diameter, made of unglazed earthenware, and therefore porous. The ends of the tube are luted to the wide tube, and two tubes, *c* and *c'*, are inserted into the ends, as shown in the drawing. With this arrangement it is possible for a gas to pass into the annular space between the walls of the two tubes, whence it can be collected. Steam from a retort or flask is passed through the tube *d* into the inner porous tube *t*. This steam on entering the red-hot space is decomposed into hydrogen and oxygen. The densities of these gases are very different, hydrogen being sixteen times lighter than oxygen.

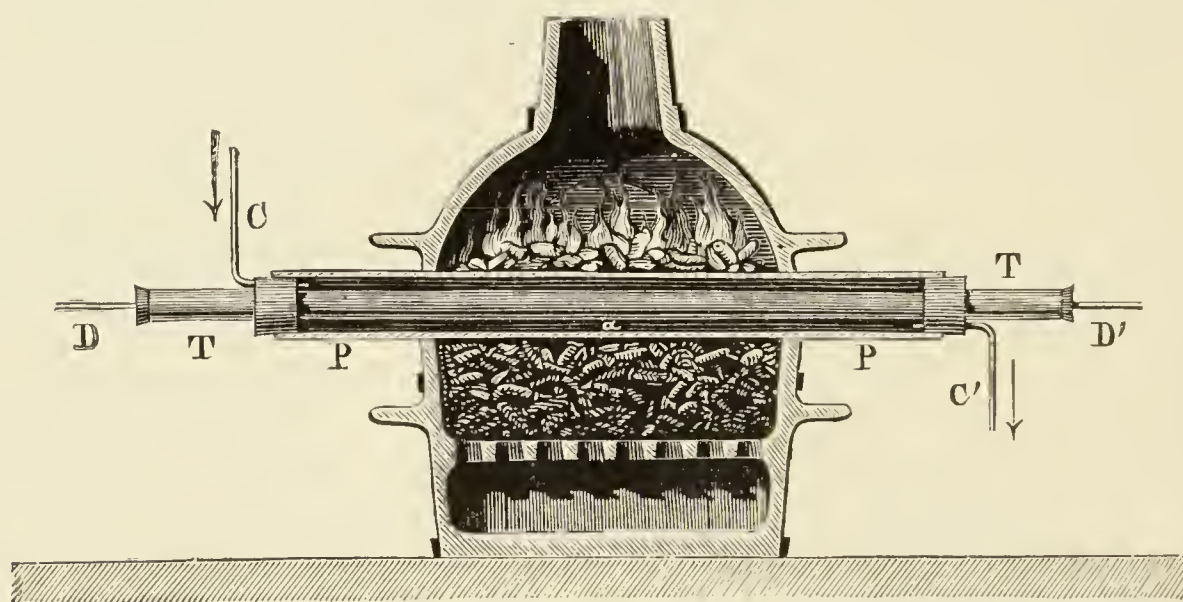


FIG. 20.—Decomposition of water by the action of heat, and the separation of the hydrogen formed by its diffusion through a porous tube.

Light gases, as we saw above, penetrate through porous surfaces very much more rapidly than denser ones, and therefore the hydrogen passes through the pores of the tube into the annular space very much more rapidly than the oxygen (about four times quicker, judging by the results of experiment). The hydrogen which separates out into the annular space can only be collected when this space does not contain any oxygen. If any air remains in this space, then the hydrogen which passes out will combine with its oxygen and form water. For this reason a gas incapable of supporting combustion—for instance, nitrogen or carbonic anhydride—is previously passed into the annular space. Thus the carbonic anhydride is passed through the tube *c*, and the hydrogen, separated from the steam, is collected through the tube *c'*, and will be partly mixed with carbonic anhydride. A certain portion of the carbonic anhydride will penetrate through the pores of the

unglazed tube into the interior of the tube T. The oxygen will remain in this tube, and the volume of the remaining oxygen will be half that of the hydrogen which separates out from the annular space.^{6a}

The decomposition of water is effected much more easily by a method of substitution, advantage being taken of the affinity of substances for either the oxygen or the hydrogen of water. If a substance be added to water, which takes up the oxygen, that is, which replaces the hydrogen, we shall then obtain the latter gas from the water. Thus with sodium, water gives hydrogen, whilst with chlorine, which takes up the hydrogen, oxygen is obtained.

Hydrogen is evolved from water by many metals, which are capable of forming oxides in air; that is, which are capable of burning or combining with oxygen. The capacity of metals for combining with oxygen, and therefore for decomposing water, or for the evolution of hydrogen, is very varied.⁷ Among metals potassium and sodium

^{6a} Part of the oxygen will also penetrate through the pores of the tube, but, as was said before, in much smaller quantity than the hydrogen; and as the density of oxygen is sixteen times greater than that of hydrogen, the volume of oxygen which passes through the porous walls will be four times less than that of the hydrogen (the quantities of gases passing through porous walls being inversely proportional to the square roots of their densities). The oxygen which separates out into the annular space will combine, when the temperature falls a certain amount, with the hydrogen; but as each volume of oxygen only requires two volumes of hydrogen, whilst four volumes of hydrogen will pass through the porous walls for every volume of oxygen that passes, part of the hydrogen will remain free, and can be collected from the annular space. A corresponding quantity of oxygen remaining from the decomposition of the water can be collected from the inner tube.

⁷ In order to demonstrate the differences between the affinities of oxygen for different elements, it suffices to compare the amounts of heats evolved in their combination with 16 parts by weight of oxygen; in the case of sodium (when Na_2O is formed, or 46 parts of Na combine with 16 parts of oxygen, according to Beketoff) 100,000 calories (or kilogram units of heat) are evolved, for hydrogen (when water, H_2O , is formed) 69,000 calories, for magnesium (MgO is formed) about 140, for aluminium ($\frac{1}{3}\text{Al}_2\text{O}_3$ is formed) about 130, for iron (when the oxide FeO is formed) 69,000, or (if the oxide Fe_2O_3 is formed) 64,000 calories, for zinc (forming ZnO) 86,000 calories, for lead (when PbO is formed) 51,000 calories, for copper (when CuO is formed) 38,000 calories, and for mercury (HgO being formed) 31,000 calories.

These figures cannot correspond directly with the magnitudes of the affinities, for the physical and mechanical side of the matter is very different in the different cases. Hydrogen is a gas, and, in combining with oxygen, gives a liquid; consequently it changes its physical state, and in doing so evolves heat. But zinc and copper are solids, and, in combining with oxygen, give solid oxides. The oxygen, previously a gas, now passes into a solid or liquid state, and so must also give up its store of heat in forming oxides. Therefore the figures expressing the heat of combination cannot depend only upon the affinities, i.e., only on the loss of internal energy previously in the elements. Nevertheless the figures above cited correspond, in a certain degree, with the order in which the elements stand in respect to their affinity for oxygen, as may be seen from the fact that mercury oxide, which evolves the least heat (among the above examples), is the least stable and is easily decomposed, giving up its oxygen; whilst sodium, the formation of whose oxide is accompanied by the greatest evolution of heat, is able to decompose all

exhibit considerable energy in this respect. The first occurs in potash, the second in soda. They are both lighter than water, soft, and readily change in air. By bringing one or the other of them into contact with water at the ordinary temperature⁸ a quantity of hydrogen, corresponding with the amount of the metal taken, may be directly obtained. One gram of hydrogen, occupying a volume of 11.16 litres at 0° and 760 mm., is evolved for every 39 grams of potassium or 23 grams of sodium taken. The phenomenon may be observed in the following

the other oxides, taking up their oxygen. In order to generalise the connection between affinity and the evolution and absorption of heat, which is evident in its main features, and was firmly established by the researches of Favre and Silberman (about 1840), and then of Thomsen (in Denmark) and Berthelot (in France), many investigators, especially the one last mentioned, established the *law of maximum work*. This states that only those chemical reactions take place of their own accord in which the greatest amount of chemical (latent, potential) energy is transformed into heat. But, in the first place, we are not able, judging from what has been said above, to distinguish that heat which corresponds with purely chemical action from the sum total of the heat observed in a reaction (in the calorimeter); in the second place, there are evidently endothermal reactions which proceed under the same circumstances as exothermal ones (carbon burns in the vapour of sulphur with absorption of heat, whilst in oxygen it evolves heat); and, in the third place, there are reversible reactions, which when taking place in one direction evolve heat, and when taking place in the opposite direction, absorb it; and, therefore, the principle of maximum work in its elementary form is not supported by science. But the subject continues to be developed, and will probably lead to a general law, such as thermal chemistry does not at present possess. And now thermochemical data clearly show that the chemical affinity of sodium for oxygen is greater than that of hydrogen, whilst mercury and copper have less affinities for oxygen than hydrogen has. Hence sodium easily decomposes water, which neither mercury nor copper can do. If aluminium does not decompose water directly, it is only because the oxide Al_2O_3 is insoluble in water, and a coating of the hydrogen formed prevents the reaction (Ditte). This and many other instances show that the course of chemical reactions is determined, not only by the properties and energy of the reacting substances, but also by the nature of those produced.

⁸ If a piece of metallic sodium be thrown into water, it floats on it (owing to its lightness), keeps in a state of continual motion (owing to the evolution of hydrogen on all sides), and immediately decomposes the water, evolving hydrogen, which can be ignited. This experiment may, however, lead to an explosion should the sodium stick to the walls of the vessel, and begin to act on the limited mass of water immediately adjacent to it (probably in this case the NaHO and Na yield Na_2O , which acts on the water, evolving much heat and rapidly forming steam), and the experiment should therefore be cautiously performed. The decomposition of water by sodium may be demonstrated better, and with greater safety, in the following manner. Into a glass cylinder filled with mercury, and immersed in a mercury bath, water is first introduced, and owing to its lightness rises to the top, and then a piece of sodium wrapped in paper is introduced into the cylinder by means of forceps. The metal rises through the mercury to the surface of the water, on which it remains, and evolves hydrogen, which collects in the cylinder and may be tested after the experiment has been completed. The safest method of making this experiment is, however, as follows. The sodium (cleaned from the naphtha in which it is kept) is either wrapped in fine copper gauze and held by forceps or else held in forceps to the end of which a small copper cage is attached, and is then held under water. The evolution of hydrogen goes on quietly, and the gas may be collected in a bell jar and then lighted.

way. A solution of sodium in mercury—or ‘sodium amalgam,’ as it is generally called—is poured into a vessel containing water, where, owing to its weight, it sinks to the bottom; the sodium held in the mercury then acts on the water like pure sodium, liberating hydrogen. The mercury does not act here, and the same amount of it as was taken for dissolving the sodium is obtained in the residue. The hydrogen is evolved gradually in the form of bubbles, which pass through the liquid.

Beyond the hydrogen evolved and a solid substance which remains in solution (and may be obtained by evaporating the resultant liquid) no other products are here obtained. Consequently from the two substances (water and sodium) taken the same number of new substances (hydrogen and the substance dissolved in water, namely, caustic soda) have been obtained, from which we may conclude that the reaction which here takes place is one of double decomposition or of substitution. The resultant solid is nothing else than the so-called caustic soda (sodium hydroxide), which is made up of sodium, oxygen, and half of the hydrogen contained in the water. The substitution, therefore, takes place between the hydrogen and the sodium, half of the hydrogen in the water being replaced by the sodium and evolved in a free state. Hence the reaction which takes place here may be expressed by the equation: $\text{H}_2\text{O} + \text{Na} = \text{NaHO} + \text{H}$; the meaning of this is clear from what has already been said.⁹

⁹ This reaction is vigorously exothermal, i.e., it is accompanied by the evolution of heat. If a sufficient quantity of water be taken, the whole of the sodium hydroxide, NaHO, formed is dissolved, and about 42,500 kilogram units of heat are evolved per 23 grams of sodium taken. As 40 grams of sodium hydroxide are produced, and they in dissolving, judging from direct experiment, evolve about 10,000 calories, the reaction would evolve about 32,500 calories, supposing no excess of water to be present and no solution to be formed. We shall afterwards learn that hydrogen contains, in its smallest isolable particles, H_2 and not H , so that the reaction should be written thus, $2\text{Na} + 2\text{H}_2\text{O} = \text{H}_2 + 2\text{NaHO}$, and it then corresponds with an evolution of heat of + 65,000 calories. And as N. N. Beketoff showed that Na_2O , or anhydrous oxide of sodium, combines with water, forming the hydrate, or sodium hydroxide (caustic soda), 2NaHO , with the evolution of about 35,500 calories, the reaction $2\text{Na} + \text{H}_2\text{O} = \text{H}_2 + \text{Na}_2\text{O}$ corresponds to 29,500 calories. This quantity of heat is less than that which is evolved by the oxide in combining with water and forming caustic soda, and therefore it is not to be wondered at that the hydrate, NaHO, is always formed and not the anhydrous substance Na_2O . That such a conclusion, agreeing with the facts, is inevitable is also seen from the fact that, according to Beketoff, the anhydrous sodium oxide, Na_2O , acts directly on hydrogen, with separation of sodium, $\text{Na}_2\text{O} + \text{H} = \text{NaHO} + \text{Na}$. This reaction is accompanied by an evolution of heat equal to about 3,000 calories, because $\text{Na}_2\text{O} + \text{H}_2\text{O}$ gives, as we saw, 35,500 calories and $\text{Na} + \text{H}_2\text{O}$ evolves 32,500 calories. However, an opposite reaction also takes place— $\text{NaHO} + \text{Na} = \text{Na}_2\text{O} + \text{H}$ (both with the aid of heat)—in which of course heat is absorbed. In this we see an example of calorimetric calculations and the limited application of the law of maximum work to the general phenomena of reversible reactions, to which the case just considered belongs.

Sodium and potassium act on water at the ordinary temperature. Other heavier metals only act on it at higher temperatures, and even then not so rapidly or vigorously. Thus magnesium and calcium only liberate hydrogen from water at its boiling-point, and zinc and iron only at a red heat; whilst a whole series of heavy metals, such as copper, lead, mercury, silver, gold, and platinum, do not in the least decompose water at any temperature, and do not replace its hydrogen.

From this it is clear that hydrogen may be obtained by the decomposition of steam by the action of iron (or zinc) at a high temperature. The experiment is conducted in the following manner. Pieces of iron (filings, nails, &c.) are placed in a porcelain tube, which is then subjected to a strong heat and steam passed through it. The steam, coming into contact with the iron, gives up its oxygen to it, the hydrogen being thus set free and passing out at the other end of the tube, together with undecomposed steam. This method, which is historically of great importance,¹⁰ is practically inconvenient, as it requires a rather high temperature. Further, this reaction, as a reversible one (a red-hot mass of iron decomposes a current of steam, forming oxide and hydrogen; and a mass of oxide of iron, heated to redness in a stream of hydrogen, forms iron and steam), does not proceed in virtue of the comparatively small difference between the affinities of oxygen for iron (or zinc) and for hydrogen, but only because the hydrogen escapes, as it is formed, by virtue of its elasticity.¹¹ If the oxygen compounds—that is, the oxides—which are obtained

¹⁰ The composition of water, as we saw above, was determined by passing steam over red-hot iron. The same method was formerly used for making hydrogen for filling balloons. An oxide having the composition Fe_3O_4 is formed in the reaction, which is hence expressed by the equation, $3\text{Fe} + 4\text{H}_2\text{O} = \text{Fe}_3\text{O}_4 + 8\text{H}$.

¹¹ The reaction between iron and water (notes 7 and 10) is reversible. By heating the oxide in a current of hydrogen, water and iron are obtained. From this it follows, from the principle of chemical equilibria, that if iron and hydrogen be taken, and also oxygen in such quantity that it is insufficient for combination with both substances, then it will divide itself between the two: part of it will combine with the iron and the other part with the hydrogen, but a portion of both of these will remain in an uncombined state.

Therefore, if iron and water be placed in a closed space, decomposition of the water will proceed on heating to the temperature at which the reaction, $3\text{Fe} + 4\text{H}_2\text{O} = \text{Fe}_3\text{O}_4 + 8\text{H}$, commences; it does not go on to the end but ceases, because the conditions for the reverse reaction are attained, and a state of equilibrium will ensue after the decomposition of a certain quantity of water. Here, again, the reversibility is connected with the small heat effect, and again both reactions (direct and reverse) proceed at a red heat. But if, in the above-described reaction, the hydrogen escapes as it is evolved, then its partial pressure does not increase with its formation, and therefore all the iron can be oxidised by the water. In this we see the influence of mass to which we shall have occasion to return later. With copper and lead there will be no decomposition, either at the ordinary or at a high temperature, because the affinities of these metals for oxygen are much less than that of hydrogen.

from the iron or zinc be able to pass into solution, then the affinity acting during solution is added, and the reaction may become non-reversible and proceed with comparatively much greater facility.¹² As the oxides of iron and zinc, by themselves insoluble in water, are capable of combining with (have an affinity for) acid oxides (as we shall afterwards fully consider), and form saline and soluble substances with acids or hydrates having acid properties, these metals are able by the action of such acid hydrates, or of their aqueous solutions,¹³ to liberate hydrogen with great ease at the ordinary temperature ; that is, they act on solutions of acids just as sodium acts on water.¹⁴ Sulphuric acid, H_2SO_4 , is usually chosen for this purpose ; the hydrogen is displaced from it by many metals with much greater facility than directly from water, and such a displacement is accompanied by the evolution of a large amount of heat.¹⁵ When the hydrogen in sulphuric acid

¹² In general, if reversible as well as non-reversible reactions can take place between substances acting on each other, then, judging by our present knowledge, the non-reversible reactions take place in the majority of cases, which obliges one to acknowledge the action, in this case, of comparatively strong affinities. The reaction, $\text{Zn} + \text{H}_2\text{SO}_4 = \text{H}_2 + \text{ZnSO}_4$, which takes place in solutions at the ordinary temperature, is scarcely reversible under these conditions, but at a certain high temperature, it becomes reversible, because then zinc sulphate and sulphuric acid decompose, and the action must take place between the water and zinc. From the preceding proposition results proceed which are in some cases verified by experiment. If the action of zinc or iron on a solution of sulphuric acid is a non-reversible reaction, we may by its means obtain hydrogen in a very compressed state, and compressed hydrogen will not act on solutions of sulphates of the above-named metals. This was actually verified as far as it was possible, in the experiments, to keep up the compression or pressure of the hydrogen. Those metals which do not evolve hydrogen with acids, on the contrary, should, at least with increase of pressure, be displaced by hydrogen. And in fact Brunner showed that gaseous hydrogen displaces platinum and palladium from the aqueous solutions of their chlorine compounds, but not gold, and Beketoff succeeded in showing that silver and mercury, under a considerable pressure, are separated from the solutions of certain of their compounds by means of hydrogen. Reaction commences under a pressure of only six atmospheres if a weak solution of silver sulphate be taken ; with a stronger solution a much greater pressure is, however, required for the separation of the silver.

¹³ For the same reason, many metals in acting on solutions of the alkalies displace hydrogen. Aluminium acts particularly well in this respect, because its oxide gives a soluble compound with alkalies. For the same reason tin, in acting on hydrochloric acid, evolves hydrogen, and silicon does the same with hydrofluoric acid.

¹⁴ It is acknowledged that zinc itself acts on water, even at the ordinary temperature, but that the action is confined to small masses and only proceeds at the surface. In reality, zinc, in the form of a very fine powder, or so-called 'zinc dust,' is capable of decomposing water with the formation of oxide (hydrated) and hydrogen. The oxide formed acts on sulphuric acid, water then dissolves the salt produced, and the action continues because one of the products of the action of water on zinc, namely, the zinc oxide, is removed from the surface. One might naturally imagine that the reaction does not proceed directly between the metal and the water, but between the metal and the acid ; but such a simple representation, which we shall notice later, hides the mechanism of the reaction, and does not permit of its actual complexity being seen.

¹⁵ According to Thomsen, the reaction between zinc and a very weak solution of sulphuric acid evolves about 38,000 calories (zinc sulphate being formed) per 65 parts

is replaced by a metal, a substance is obtained which is called a salt of sulphuric acid or a sulphate. Thus, by the action of zinc on sulphuric acid, hydrogen and zinc sulphate, ZnSO_4 ,^{15a} are obtained. The latter is a solid substance, soluble in water. In order that the action of the metal on the acid should go on regularly, and to the end, it is necessary that the acid should be diluted with water, which dissolves the salt as it is formed; otherwise the salt in a solid state covers the metal and prevents the acid from attacking it. Usually the acid is diluted with from three to five times its volume of water, and the metal is covered with this solution. In order that the metal may act rapidly on the acid it should present a large surface, so that a maximum amount of the reacting substances may come into contact in a given time. For this

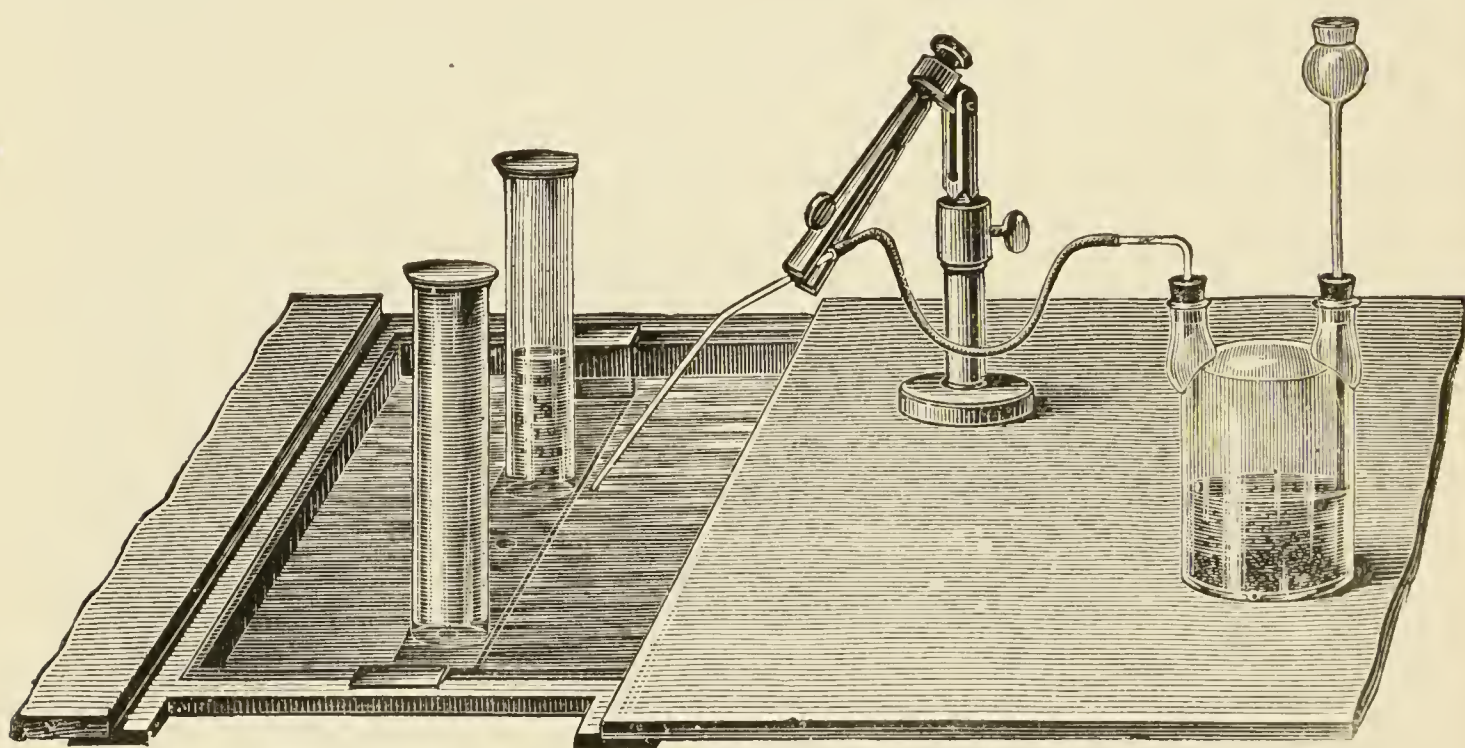


FIG. 21.—Apparatus for the preparation of hydrogen from zinc and sulphuric acid.

purpose the zinc is used as strips of sheet zinc, or in the granulated form (that is, zinc which has been poured from a height, in a molten state, into water). The iron should be in the form of wire, nails, filings, or cuttings.

by weight of zinc; and 56 parts by weight of iron—which combine, like 65 parts of zinc, with 16 parts by weight of oxygen—evolve about 25,000 calories forming ferrous sulphate, FeSO_4). Paracelsus observed the action of metals on acids in the seventeenth century; but it was not until the eighteenth century that Lémery determined that the gas evolved in this action is a particular one which differs from air and is capable of burning. Even Boyle confused it with air. Cavendish determined the chief properties of the gas discovered by Paracelsus. At first it was called ‘inflammable air:’ later, when it was recognised that in burning it gives water, it was called hydrogen, a word derived from the Greek terms for water and generator.

^{15a} If, when the sulphuric acid is poured over the zinc, the evolution of the hydrogen proceed too slowly, it may be greatly accelerated by adding a small quantity of a solution of copper sulphate or platinum chloride to the acid. The reason of this is explained in Chap. XVI., note 10a.

The usual method of obtaining hydrogen is as follows. A certain quantity of granulated zinc is put into a double-necked, or Woulfe's, bottle. Into one neck a funnel is placed, reaching to the bottom of the bottle, so that the liquid poured in may prevent the hydrogen from escaping through it. The gas escapes through a special gas-conducting tube, which is firmly fixed, by a cork, into the other neck, and ends in a water-bath (fig. 21), under the orifice of a glass cylinder full of water.¹⁶ If sulphuric acid be now poured into the Woulfe's bottle it will

¹⁶ As laboratory experiments with gases require special methods of manipulation, we will describe certain of them here. When in laboratory practice an intermittent supply of hydrogen (or other gas which is evolved without the aid of heat) is required, the apparatus represented in fig. 22 is the most convenient. It consists of two bottles, having at the bottom orifices, in which corks with tubes are placed, and these tubes are connected by an indiarubber tube (sometimes furnished with a spring clamp). Zinc is placed in

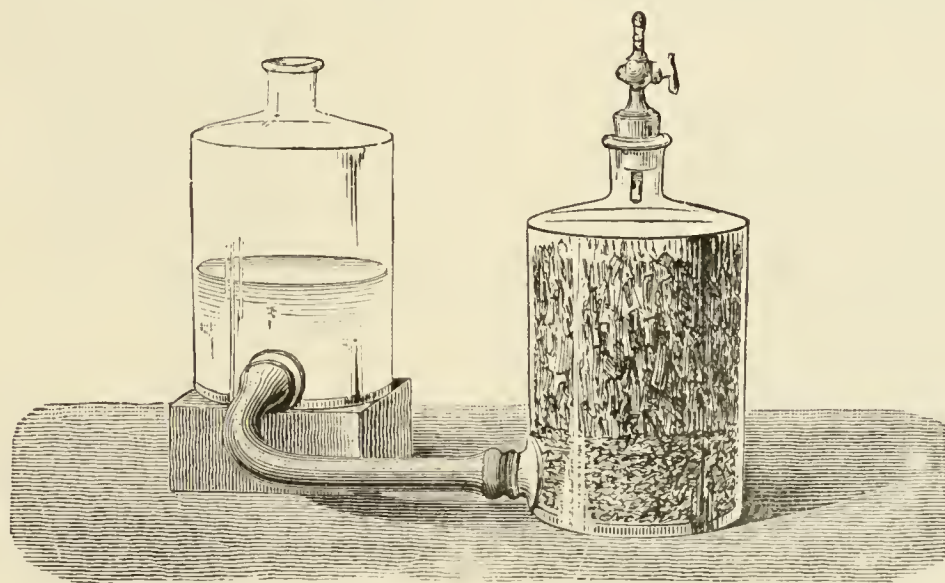


FIG. 22.—A very convenient apparatus for the preparation of gases obtained without heat. It may also replace an aspirator or gasometer.

one bottle and dilute sulphuric acid in the other. The neck of the former is closed by a cork fitted with a gas-conducting tube with a stopcock. If the two bottles be connected with each other, and the stopcock be opened, the acid will flow to the zinc and evolve hydrogen. If the stopcock be closed, the hydrogen will force out the acid from the bottle containing the zinc, and the action will cease. Or the vessel containing the acid may be placed at a lower level than that containing the zinc, when all the liquid will flow into it; and in order to start the action the acid vessel may be placed on a higher level than the other, when the acid will flow to the zinc. It can also be employed for collecting gases (as an aspirator or gasometer).

An *aspirator* (for collecting and delivering gas) usually consists of a vessel furnished with a stopcock at the bottom. A stout cork, through which a glass tube passes, is fixed into the neck of this vessel. If the vessel be filled up with water to the cork, and the bottom stopcock opened, the water will run out and draw gas in. For this purpose the glass tube is connected with the apparatus from which it is desired to pump out or exhaust the gas.

The aspirator represented in fig. 23 may be recommended for its continuous action. It consists of a tube, *d*, which widens out at the top, the lower part being long and narrow. In the expanded upper portion, *c*, two tubes are sealed: one, *e*, is for drawing in the gas, whilst the other, *b*, is connected with the water supply, *w*. The amount of water supplied through the tube *b* must be less than the amount which can be carried off by the tube *d*.

soon be seen that bubbles of a gas are evolved, which is hydrogen. The first part of the gas evolved should not be collected, as it is mixed

Owing to this the water in the tube *d* will flow through it in cylindrical portions alternating with cylindrical gas bubbles, which will be thus carried away. The gas which is drawn through may be collected from the end of the tube *d*; but this form of pump is usually employed where the air or gas aspirated is not to be collected. If the tube *d* is of considerable length, say 40 ft. or more, a very fair vacuum will be produced, the amount

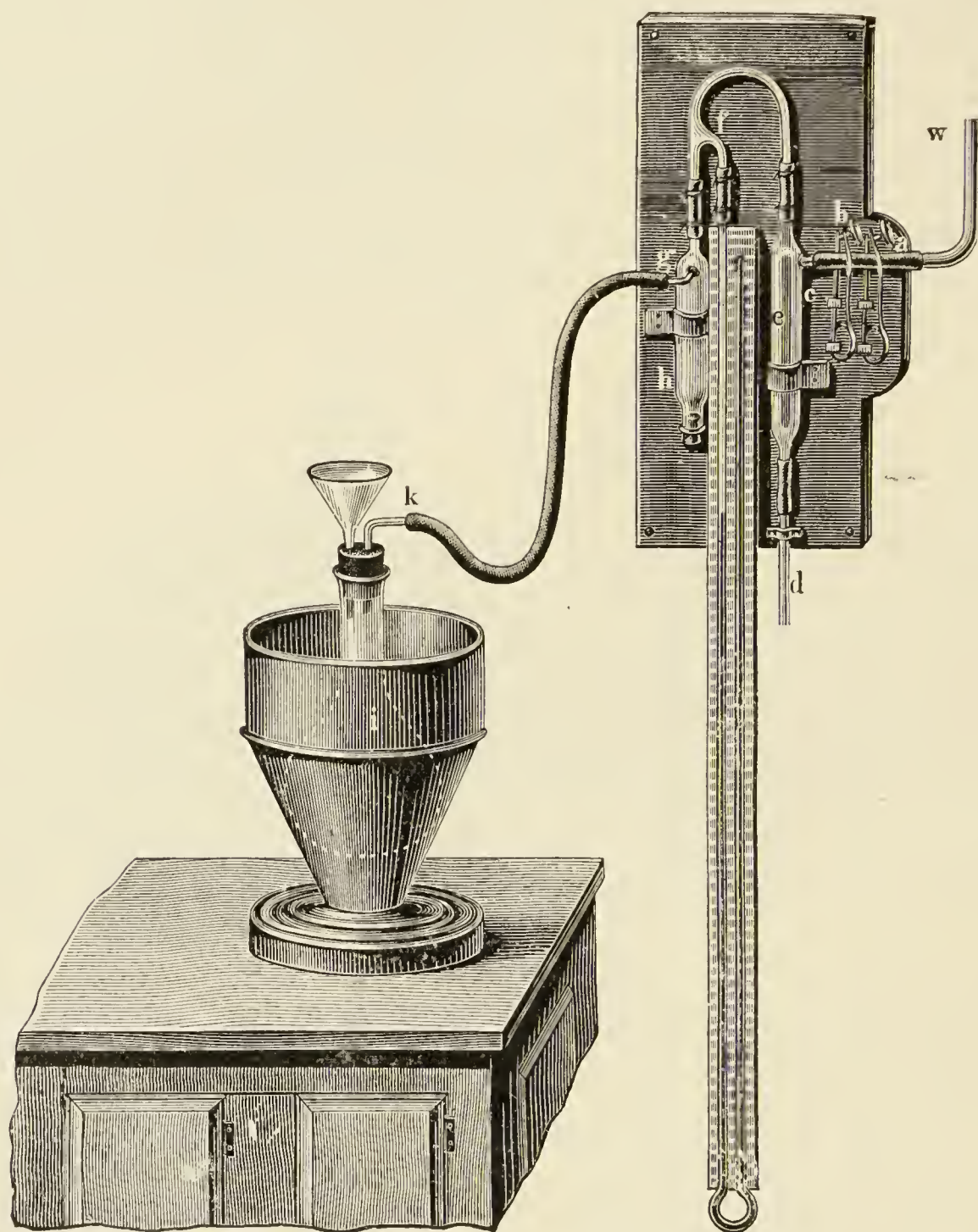


FIG. 23.—Continuous aspirator. The tube *d* should be more than 32 feet long.

being shown by the gauge *g*: it is often used for filtering under reduced pressure, as shown in the figure. If the water be replaced by mercury, and the length of the tube *d* be greater than 760 mm., the aspirator may be employed as an air-pump, and all the air may be exhausted from a limited space; for instance, by connecting *g* with a hollow sphere.

Gasholders are often used for collecting and holding gases. They are made of glass, copper, or tin plate. The usual form is shown in fig. 24. The lower vessel *B* is made hermetically tight—i.e., impervious to gases—and is filled with water. A funnel is attached to this vessel (by several supports). The vessel *B* communicates with the

with the air originally in the apparatus. This precaution should be taken in the preparation of all gases. Time must be allowed for the gas evolved to displace all the air from the apparatus, otherwise in testing the combustibility of the hydrogen an explosion may occur owing to the formation of detonating gas (the mixture of the oxygen of the air with the hydrogen).¹⁷

bottom of the funnel by a stopcock *b* and a tube *a*, reaching to the bottom of the vessel *B*. If water be poured into the funnel, and the stopcocks *a* and *b* be opened, the water will run through *a*, and the air escape from the vessel *B* by *b*. A glass tube *f* runs up the side of the vessel *B*, with which it communicates at the top and bottom, and shows the amount of water and gas the gasholder contains. In order to fill the gasholder with a gas, it is first filled with water, the cocks *a*, *b*, and *e* are closed, the nut *d* unscrewed, and the end of the tube conducting the gas from the apparatus in which it is generated is passed into *d*. As the gas fills the gasholder the water runs out at *d*. If the pressure of a gas be not greater than the atmospheric pressure, and it be required to collect it in the gasholder, then the stopcock *e* is put into communication with the space containing the gas. Then, having opened the orifice *d*, the gasholder acts like an aspirator; the gas will pass through *e*, and the water run out at *d*. If the cocks be closed, the gas collected in the gasholder may be easily preserved and transported. If it be desired to transfer this gas into another vessel, a gas-conducting tube is attached to *e*, the cock *a* opened, *b* and *d* closed, and the gas will then pass out at *e*, its pressure in the apparatus being greater than the atmospheric pressure, owing to the pressure of the water poured into the funnel. If it be required to fill a cylinder or flask with the gas, it is filled with water and inverted in the funnel, and the stopcocks *b* and *a* opened. Then water will run through *a*, and the gas will escape from the gasholder into the cylinder through *b*.

¹⁷ When it is required to prepare hydrogen in large quantities for filling balloons, copper vessels or wooden casks lined with lead are employed: they are filled with scrap iron over which dilute sulphuric acid is poured. The hydrogen generated from a number of casks is carried through lead pipes into special casks containing water (in order to cool the gas) and lime (in order to remove acid fumes). To avoid loss of gas all the joints are made hermetically tight with cement or tar. In order to fill his gigantic balloon (of 25,000 cubic metres capacity), Giffard, in 1878, constructed a complicated apparatus for giving a continuous supply of hydrogen, in which a mixture of sulphuric acid and water was run continuously into vessels containing iron, and from which the solution of iron sulphate formed was continually drawn off. When coal gas, extracted from coal, is employed for filling balloons, it should be as light, or as rich in hydrogen, as possible. For this reason, only the last portions of the gas coming from the retorts are collected,

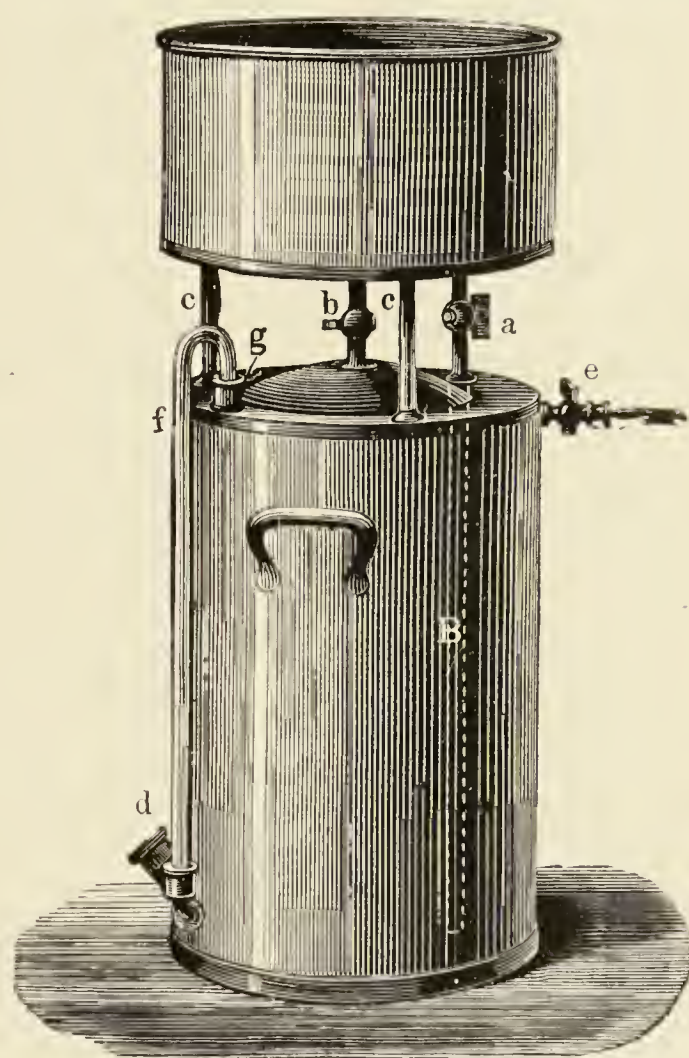


FIG. 24.—Gasholder.

Besides being contained in water, hydrogen is also present in many other substances,¹⁸ and may be obtained from them. As examples of this it may be mentioned: (1) that a mixture of formate of sodium, CHNaO_2 , and caustic soda, NaHO , when heated to redness, forms sodium carbonate, Na_2CO_3 , and hydrogen, H_2 ; ¹⁹ (2) that a number of organic substances are decomposed at a red heat, forming hydrogen, among other gases; and thus it is that hydrogen is contained in ordinary coal gas; (3) charcoal liberates hydrogen from steam at a high temperature,²⁰ but the reaction which here takes place is distinguished by its complexity, and will therefore be considered later; (4) that a certain amount of hydrogen is formed, together with other gases, in the process of decay (change under the influence of micro-organisms) of certain organic substances (for instance, of plants under water).

Gaseous hydrogen is rarely met with in nature. It has been found in the gases of volcanoes (and fumaroles), in small cavities in crystals of rock salt (under pressure and mixed with other gases), and it even occurs in small quantities in the atmosphere, according to the careful and, besides this, it is then sometimes passed through red-hot vessels, in order to decompose the hydrocarbons as much as possible. Charcoal is deposited in these vessels, and hydrogen remains as gas. Coal gas may be yet further enriched in hydrogen, and consequently rendered lighter, by passing it over an ignited mixture of charcoal and lime.

L. Mond (London) proposes to manufacture hydrogen on a large scale from water gas (see *infra*, and Chapters VIII. and IX.), which contains a mixture of oxide of carbon (CO) and hydrogen, and is produced by the action of steam upon incandescent coke ($\text{C} + \text{H}_2\text{O} = \text{CO} + \text{H}_2$). He destroys the oxide of carbon by converting it into carbon and carbonic anhydride, $2\text{CO} = \text{C} + \text{CO}_2$, which is easily done by means of incandescent finely divided metallic nickel; the carbon then remains with the nickel, from which it may be removed by burning it in air, and the nickel can then be used over again (see Chapter IX., note 24a). The CO_2 formed is removed from the hydrogen by passing it through milk of lime. This process should apparently give hydrogen on a large scale more economically than any of the methods hitherto proposed. Hydrogen is formed in many other ways. We shall meet many reactions which are accompanied by the formation of hydrogen gas. The methods here mentioned are the most convenient and easily adopted.

¹⁸ Of the metals, only a very few combine with hydrogen (for example, palladium and sodium), and give substances which are easily decomposed, and some metals, especially platinum and iron, absorb this gas (see Occlusion, note 37). Of the non-metals, the halogens (fluorine, chlorine, bromine, and iodine) most easily form hydrogen compounds: of these the hydrogen compound of chlorine, and still more that of fluorine, are stable, whilst those of bromine and iodine are easily decomposed, especially the latter. The other non-metals—for instance, sulphur, carbon, and phosphorus—give hydrogen compounds of varying composition and properties, but they are all less stable than water.

¹⁹ This reaction, expressed by the equation, $\text{CNaHO}_2 + \text{NaHO} = \text{CNa}_2\text{O}_3 + \text{H}_2$, may be effected in a glass vessel, like the decomposition of copper carbonate or mercury oxide (see Introduction): it is non-reversible, and takes place without the presence of water, and therefore Pictet (see later) made use of it to obtain hydrogen under great pressure.

²⁰ The reaction between charcoal and superheated steam is a double one—that is, there may be formed either carbonic oxide, CO (according to the equation, $\text{H}_2\text{O} + \text{C} = \text{H}_2 + \text{CO}$), or carbonic anhydride, CO_2 (according to the equation $2\text{H}_2\text{O} + \text{C} = 2\text{H}_2 + \text{CO}_2$), and the resulting mixture is called *water-gas*, but of this we shall speak in Chapter IX.

researches of Armand Gautier (1900). The spectroscope has proved that hydrogen is also undoubtedly present in the atmospheres of the sun and many of the stars (Chap. XIII.).

The properties of hydrogen.—Hydrogen presents us with an example of a gas which at first sight does not differ from air. It is not surprising, therefore, that Paracelsus, having discovered that an aëriiform substance is obtained by the action of metals on sulphuric acid, did not determine exactly its difference from air.^{20a} In fact, hydrogen, like air, is colourless, and has no smell;²¹ but a more intimate acquaintance with its properties proves it to be entirely different from air. The first sign which distinguishes hydrogen from air is its combustibility. This property is so easily observed that it is the one to which recourse is usually had in order to recognise if hydrogen is evolved in a reaction, although there are many other combustible gases. But before speaking of the combustibility and other chemical properties of hydrogen, we will first describe the physical properties of this gas, as we did in the case of water. It is easy to show that it is one of the lightest gases.²²

^{20a} Considering the immense velocity of the hydrogen molecules—about 1,800 metres a second (see Chapter I., note 34)—they may, perhaps, travel away from the terrestrial atmosphere into space. The absence of any considerable quantity of hydrogen in the atmosphere of the earth is also probably due to its being converted into water by electrical discharges, &c., in the presence of an excess of oxygen.

²¹ Hydrogen obtained by the action of zinc or iron on sulphuric acid generally smells of hydrogen sulphide (like rotten eggs), which it contains in admixture. As a rule, such hydrogen is not so pure as that obtained by the action of an electric current or of sodium on water. The impurity of the hydrogen depends on the impurities contained in the zinc, or iron, and sulphuric acid, and on secondary reactions which take place simultaneously with the main reaction. Impure hydrogen may be freed from the impurities it contains: some of them—namely, those having acid properties—are absorbed by caustic soda, and may therefore be removed by passing the gas through a solution of this substance; another series of impurities is absorbed by a solution of mercuric chloride; and, lastly, a third series is absorbed by a solution of potassium permanganate. If absolutely **pure hydrogen** be required, it is sometimes obtained by the decomposition of water (previously boiled to expel all air, and mixed with pure sulphuric acid) by the galvanic current. Only the gas evolved at the negative electrode is collected. Or else an apparatus like that which gives detonating gas is used, the positive electrode, however, being immersed under mercury containing zinc in solution. The oxygen which is evolved at this electrode then combines immediately, at the moment of its evolution, with the zinc, and this compound dissolves in the sulphuric acid and forms zinc sulphate, which remains in solution, so that the hydrogen generated will be free from oxygen. Quite pure hydrogen (and oxygen) is obtained by decomposing a solution of caustic baryta by electricity. Caustic soda gives hydrogen containing some carbonic anhydride, and sulphuric acid also does not give perfectly pure gases. (Becker, 1902.)

²² An inverted beaker is attached to one arm of the beam of a tolerably sensitive balance, and its weight counterpoised by weights in the pan attached to the other arm. If the beaker be then filled with hydrogen it rises, owing to the air being replaced by hydrogen. At the ordinary temperature of a room, a litre of air weighs about 1·2 gram, and on replacing the air by hydrogen a decrease in weight of about 1 gram per litre is obtained. Moist hydrogen is heavier than dry—for aqueous vapour is nine times heavier than hydrogen. In filling balloons it is usually calculated (as it is impossible to have

If passed into the bottom of a flask full of air, hydrogen will not remain in it, but, owing to its lightness, rapidly escapes and mixes with the atmosphere. If, however, a cylinder whose orifice is turned downwards be filled with hydrogen, it will not escape, or, more correctly, it will only slowly mix with the atmosphere. This may be demonstrated by the fact that a lighted taper sets fire to the hydrogen at the orifice of the cylinder, and is itself extinguished inside the cylinder. Hence hydrogen, being itself combustible, does not support combustion. The great lightness of hydrogen is taken advantage of for balloons. Ordinary coal gas, which is often also used for the same purpose, is only about twice as light as air, whilst hydrogen is fourteen times lighter than air. A very simple experiment with soap bubbles illustrates very well the application of hydrogen to the filling of balloons. Charles, of Paris, showed the lightness of hydrogen in this way, and constructed a balloon filled with hydrogen almost simultaneously with Montgolfier. One litre of pure and dry hydrogen ²³ at 0° and 760 mm. pressure weighs 0.08995 gram; that is, hydrogen is almost 14½ times lighter than air. It is the lightest of all gases. The small density of hydrogen determines many remarkable properties which it shows; thus hydrogen passes exceedingly rapidly through fine orifices, its molecules (Chap.

perfectly dry hydrogen or to obtain it quite free from air) that the lifting force due to the difference between the weights of equal volumes of hydrogen and air is equal to 1 kilogram (=1,000 grams) per cubic metre (=1,000 litres).

²³ The density of hydrogen in relation to the air has been repeatedly determined. The first determination, made by Lavoisier, was not very exact. Taking the density of air as unity, he obtained 0.0769 for that of hydrogen; that is, this gas is thirteen times lighter than air. More accurate determinations are due to Thomsen, who obtained the figure 0.0693; Berzelius and Dulong, who obtained 0.0688; and Dumas and Boussingault, who obtained 0.06945. Regnault, and more recently Le Duc, took two spheres of considerable volume, having equal capacities and displacing equal volumes of air (thus avoiding the necessity of any correction for weighing them in air). Both spheres were attached to the scale pans of a balance. One was sealed up, and the other weighed first empty and then full of hydrogen. Thus, knowing the weight of the hydrogen filling the sphere, and the capacity of the sphere, it was easy to find the weight of a litre of hydrogen; and, knowing the weight of a litre of air at the same temperature and pressure, it was easy to calculate the density of hydrogen. Regnault found the average density of hydrogen to be 0.06926; Le Duc, 0.06948. In 1892 and 1895 Rayleigh, Morley, and Thomsen made fresh determinations, and obtained results very nearly equal to the above. The mean of their results is equal to 0.06956, and this latter figure must now be looked upon as near the truth. Hydrogen is therefore 14.4 times lighter than air. In other words a litre of hydrogen at 0°, under the normal pressure of 760 mm., at the sea level and latitude 45°, weighs 0.08995 gram, or at t° , and under the pressure H , at latitude 45°, the weight of a litre of hydrogen is equal to

$$0.08995 \frac{H}{760} \times \frac{1}{1 + 0.00367t} \text{ grams.}$$

In this book we shall always refer the density of gases to that of hydrogen, as it is the lightest of all gases and vapours under the same conditions.

I.) being endowed with the greatest velocity.²⁴ At pressures somewhat higher than that of the atmosphere, all other gases exhibit a greater compressibility and coefficient of expansion than they should, according to the laws of Mariotte and Gay-Lussac; whilst hydrogen, on the contrary, is compressed to a less degree than it should be from the law of Mariotte,²⁵ and with a rise of pressure it expands slightly

²⁴ If a cracked flask be filled with hydrogen, and its neck immersed under water or mercury, the liquid will rise up into the flask, owing to the hydrogen passing out through the cracks about 3·8 times quicker than the air is able to pass through these cracks into the flask. The same phenomenon may be better observed if, instead of a flask, a tube be employed whose end is closed by a porous substance, such as graphite, unglazed earthenware, or a gypsum plate.

²⁵ According to Boyle and Mariotte's law, for a given gas at a constant temperature the volume decreases by as many times as the pressure increases; that is, the product of the volume v and the pressure p for a given gas is a constant quantity: $pv = C$, which does not vary with a change of pressure. This equation does very nearly and exactly express the observed relation between the volume and pressure, but only within comparatively small variations of pressure. If these variations be in any degree considerable, the quantity pv proves to be dependent on the pressure, and it either increases or diminishes with an increase of pressure. In the former case the compressibility is less than it should be according to Mariotte's law—in the latter case it is greater. We will call the first case a positive discrepancy (because then $d(pv)/d(p)$ is greater than zero), and the second case a negative discrepancy (because then $d(pv)/d(p)$ is less than zero). Determinations made by myself (in the seventies), M. L. Kirpicheff, and V. A. Hemilian showed that all known gases at low pressures—i.e., when considerably rarefied—present positive discrepancies. On the other hand, it appears from the researches of Cailletet, Natterer, and Amagat that all gases under great pressures (when the volume obtained is 500–1,000 times less than under the atmospheric pressure) also present positive discrepancies. Thus under a pressure of 2,700 atmospheres air is compressed, not 2,700 but only 800 times, and hydrogen 1,000 times. Hence the positive kind of discrepancy is, so to speak, normal to gases. And this is easily intelligible. If a gas followed Mariotte's law, or if it were compressed to a greater extent than is shown by this law, then under great pressures it would attain a density greater than that of solid and liquid substances, which is in itself improbable and even impossible by reason of the fact that solid and liquid substances are themselves but little compressible. For instance, a cubic centimetre of oxygen at 0° and under the atmospheric pressure weighs about 0·0014 gram, and at a pressure of 3,000 atmospheres (this pressure is attained in gums) it would, if it followed Mariotte's law, weigh 4·2 grams—that is, would be about four times heavier than water—and at a pressure of 10,000 atmospheres it would be heavier than mercury. Besides this, positive discrepancies are probable because the molecules of a gas themselves must occupy a certain volume. Considering that Mariotte's law, strictly speaking, applies only to the intermolecular space, we can understand the necessity of positive discrepancies. If we designate the volume of the molecules of a gas by b (like van der Waals, see Chapter I., note 34), then it must be expected that $p(v - b) = C$. Hence $pv = C + bp$, which expresses a positive discrepancy. Supposing that for hydrogen, $pv = 1,000$, at a pressure of one metre of mercury, we obtain b , according to the results of Regnault's, Amagat's, and Natterer's experiments, as approximately 0·7 to 0·9.

Thus the increase of pv with increase of pressure must be considered as the normal law of the compressibility of gases. Hydrogen presents such a positive compressibility at all pressures, for it presents positive discrepancies, according to Regnault, at all pressures slightly above the atmospheric pressure. Hence hydrogen is, so to speak, a model gas. No other gas behaves so simply with a change of pressure. All other gases at pressures from 1 to 30 atmospheres present negative discrepancies; that is, they are

less than at the atmospheric pressure.²⁶ However, hydrogen, like air and many other gases which are permanent at the ordinary temperature,

then compressed to a greater degree than should follow from Mariotte's law, as was shown by the determinations of Regnault, which were verified when repeated by myself and Boguzsky. Thus, for example, on changing the pressure from 4 to 20 metres of mercury—that is, on increasing the pressure five times—the volume of hydrogen only decreased 4.93 times, and that of air 5.06 times.

The positive discrepancies from the law at low pressures are of particular interest, and, according to the above-mentioned determinations made by myself, Kirpicheff, and Hemilian, and verified (by two methods) by K. D. Kraevitch and Ramsay (London, 1894), they are common to all gases (even to those which are easily compressed into a liquid state, such as carbonic and sulphurous anhydrides). These discrepancies coincide with a very high rarefaction of the gas, where it is near a condition of maximum dispersion of its molecules, and perhaps presents a passage towards the substance termed 'luminiferous ether' which fills up interplanetary and interstellar space. If we suppose that gases are rarefiable only to a definite limit, after having attained which they (like solids) hardly alter in volume with a decrease of pressure, then on the one hand the passage of the atmosphere at its upper limits into a homogeneous ethereal medium becomes comprehensible, and on the other hand it would be expected that gases would, in a state of high rarefaction, present positive discrepancies from Boyle and Mariotte's law. Our present acquaintance with this province of highly rarefied gases is very limited (because direct measurements are exceedingly difficult to make, and are hampered by possible errors of experiment, which may be considerable), and its further development promises to elucidate much in respect to natural phenomena. To the three states of matter (solid, liquid, and gaseous) perhaps a fourth may yet be added, the ethereal or ultra-gaseous (as Crookes proposed), by which is understood matter in its highest possible state of rarefaction.

²⁶ The law of Gay-Lussac states that all gases in all conditions present one coefficient of expansion, 0.00367; that is, when heated from 0° to 100° they expand like air, 1,000 volumes of a gas at 0° occupying 1,367 volumes at 100°. Regnault, about 1850, showed that Gay-Lussac's law is not entirely correct, and that different gases, and also one and the same gas at different pressures, have not quite the same coefficients of expansion. Thus the expansion of air between 0° and 100° is 0.367 under the ordinary pressure of one atmosphere, but at three atmospheres it is 0.371, whilst that of carbonic anhydride is 0.37. Regnault, however, did not directly determine the change of volume between 0° and 100°, but measured the variation of pressure with the change of temperature. But since gases do not entirely follow Mariotte's law, the change of volume cannot be directly judged by the variation of pressure. The investigations carried on by myself and Kayander, about 1870, showed the variation of volume on heating from 0° to 100° under a really constant pressure. These investigations confirmed Regnault's conclusion, that Gay-Lussac's law is not absolutely accurate, and further showed (1) that the expansion per unit volume from 0° to 100° under a pressure of one atmosphere is for air 0.368, for hydrogen 0.367, for carbonic anhydride 0.373, for hydrogen bromide 0.386, &c.; (2) that for gases which are more compressible than should follow from Mariotte's law, the expansion by heat increases with the pressure—for example, for air at a pressure of three and a half atmospheres, it equals 0.371, for carbonic anhydride, at one atmosphere 0.373, at three atmospheres 0.389, and at eight atmospheres 0.413; (3) that for gases which are less compressible than should follow from Mariotte's law, the expansion by heat decreases with an increase of pressure—for example, for hydrogen at one atmosphere 0.367, at eight atmospheres 0.369, for air at a quarter of an atmosphere 0.370, at one atmosphere 0.368; and hydrogen like *air* (and other gases) is less compressed at low pressures than should follow from Mariotte's law (see note 25). Hence, hydrogen, starting from zero and rising to the highest pressures, exhibits a gradually, although only slightly, varying coefficient of expansion, whilst for air and other gases at the atmospheric and higher pressures the coefficient of expansion increases with the

does not pass into a liquid state even under the greatest possible pressures,²⁷ but is compressed into a lesser volume than would follow

increase of pressure, so long as their compressibility is greater than should follow from Mariotte's law. But when at considerable pressures this kind of discrepancy passes into the normal (see note 25), then the coefficient of expansion of all gases decreases with an increase of pressure, as is seen from the researches of Amagat. The difference between the two coefficients of expansion, for a constant pressure and for a constant volume, is explained by these relations. Thus, for example, for air at a pressure of one atmosphere the true coefficient of expansion (the volume varying at constant pressure) = 0.00368 (according to Mendeléeff and Kayander) and the variation of pressure (at a constant volume, according to Regnault) = 0.00367.

²⁷ Permanent gases are those which cannot be liquefied by an increase of pressure alone. With rise of temperature, all gases and vapours become permanent gases. As we shall afterwards learn, carbonic anhydride becomes a permanent gas at temperatures above 31°, and at lower temperatures it has a maximum pressure, and may be liquefied by pressure alone.

The liquefaction of gases, accomplished by Faraday (see Ammonia, Chapter VI.) and others, in the first half of the last century, showed that a number of substances are capable, like water, of assuming all three physical states, and that there is no essential difference between vapours and gases, the only distinction being that the boiling-points (or the temperatures at which the pressure = 760 mm.) of liquids lie above the ordinary temperature, and those of liquefied gases below, and that consequently a gas is superheated vapour, or vapour heated above the boiling-point, or removed from saturation and rarefied, having a lower pressure than that maximum which is proper to a given temperature and substance. We will here cite the **maximum pressures** of certain liquids and gases **at various temperatures**, because they may be taken advantage of for obtaining constant temperatures by changing the pressures at which boiling or the formation of saturated vapours takes place. The temperatures (according to the air thermometer) are placed on the left, and the pressures in millimetres of mercury (at 0°) on the right-hand side. Carbon bisulphide, CS₂; 0°, 127.9; 10°, 198.5; 20°, 298.1; 30°, 431.6; 40°, 617.5; 50°, 857.1. Aniline, C₆H₇N; 150°, 283.7; 160°, 387.0; 170°, 515.6; 108°, 677.2; 185°, 771.5. Mercury, Hg; 300°, 246.8; 310°, 304.9; 320°, 373.7; 330°, 454.4; 340°, 548.6; 350°, 658.0; 359°, 770.9. Sulphur, S; 395°, 300; 423°, 500; 443°, 700; 452°, 800; 459°, 900. These figures were obtained by Ramsay and Young. We may add the following boiling-points under a pressure of 760 mm. (according to the air thermometer, Callendar and Griffiths, 1891: aniline, 184°, 13; naphthalene, 217°, 94; benzophenone, 305°, 82; mercury, 356°, 76; sulphur, 444°, 53. And melting-points: tin, 231°, 68; bismuth, 269°, 22; lead, 327°, 69; and zinc, 417°, 57. These data may also be used for obtaining a constant temperature and for verifying thermometers. The pressures of liquefied gases are expressed *in atmospheres*. Sulphurous anhydride, SO₂: - 30°, 0.4; - 20°, 0.6; - 10°, 1; 0°, 1.5; + 10°, 2.3; 20°, 3.2; 30°, 5.3. Ammonia, NH₃: - 40°, 0.7; - 30°, 1.1; - 20°, 1.8; - 10°, 2.8; 0°, 4.2; + 10°, 6.0; 20°, 8.4. Carbonic anhydride, CO₂: - 115°, 0.033; - 80°, 1; - 70°, 2.1; - 60°, 3.9; - 50°, 6.8; - 40°, 10; - 20°, 23; 0°, 35; + 10°, 46; 20°, 58. Nitrous oxide, N₂O: - 125°, 0.033; - 92°, 1; - 80°, 1.9; - 50°, 7.6; - 20°, 23.1; 0°, 36.1; + 20°, 55.3. Ethylene, C₂H₄: - 140°, 0.033; - 130°, 0.1; - 103°, 1; - 40°, 13; - 1°, 42. Air: - 191°, 1; - 158°, 14; - 140°, 39. Nitrogen: N₂: - 203°, 0.085; - 193°, 1; - 160°, 14; - 146°, 32. The methods of liquefying gases (by pressure and cold) will be described under ammonia, nitrous oxide, sulphurous anhydride, and in later footnotes. We will now turn our attention to the fact that the evaporation of volatile liquids, under various, and especially under low, pressures, gives an easy means for obtaining **low temperatures**. Thus, liquefied carbonic anhydride, under the ordinary pressure, reduces the temperature to - 80°, and when it evaporates in a rarefied atmosphere (under an air-pump) at 25 mm. (= 0.033 atmosphere) the temperature, judging by the above-cited figures, falls to - 115° (Dewar). Even the evaporation of

from Mariotte's law.²⁸ From this it may be concluded that the critical temperature (absolute boiling-point) of hydrogen, and of gases resembling it,²⁹ lies very much below the ordinary temperature; that is, that

liquids of common occurrence, under low pressures easily attainable with an air-pump, may produce low temperatures, which may be again taken advantage of for obtaining still more volatile liquids. Water boiling in a vacuum becomes cold, and under a pressure of less than 4.5 mm. it freezes, because its pressure at 0° is 4.5 mm. A sufficiently low temperature may be obtained by forcing fine streams of air through common ether, carbon bisulphide, CS₂, or methyl chloride, CH₃Cl, and other similar volatile liquids. In the adjoining table are given, for certain gases, (1) the number of atmospheres necessary for their liquefaction at 15°, and (2) the boiling-points of the resultant liquids under a pressure of 760 mm.

	C ₂ H ₂	C ₂ H ₄	N ₂ O	CO ₂	H ₂ S	AsH ₃	NH ₃	HCl	CH ₃ Cl	C ₂ N ₂	SO ₂
(1)	39	56	45	50	10	8	7	25	4	4	3
(2)	-75°	-104°	-90°	-79°	-74°	-58°	-34°	-84°	-24°	-21°	-10°

²⁸ Natterer's determinations (1851-1854), together with Amagat's results (1880-1888), show that the compressibility of hydrogen, under high pressures, may be expressed by the following figures:—

p	=	1	100	1000	2500
v	=	1	0.0107	0.0019	0.0013
pv	=	1	1.07	1.9	3.25
s	=	0.11	10.3	58	85

where p is the pressure in metres of mercury, v the volume (that under a pressure of 1 metre being taken as 1), and s the weight in grams of a litre of hydrogen at 20°. If hydrogen followed Mariotte's law, then under a pressure of 2,500 metres one litre would contain not 85, but about 265 grams. It is evident from the above figures, that as the pressure increases, the weight of a litre of the gas approaches a limit which is doubtless the density of the gas when liquefied, and therefore the weight of a litre of liquid hydrogen would be near 100 grams (density about 0.1, which is less than that of all other liquids) at 20°, if liquid hydrogen could exist at that temperature.

²⁹ Cagniard de Latour, on heating ether in a closed tube to about 190°, observed that at this temperature the liquid is transformed into vapour occupying the original volume—that is, having the same density as the liquid. The further investigations made by Drion and by myself showed that every liquid has such an **absolute boiling-point**, above which it cannot exist as a liquid, and is transformed into a dense gas. In order to grasp the true signification of this absolute boiling temperature, it must be remembered that the liquid state is characterised by a cohesion of the particles which does not exist in vapours and gases. The cohesion of liquids is expressed in their capillary phenomena (drop formation, rise in capillary tubes, &c.), and the product of the density of a liquid into the height to which it rises in a capillary tube (of a definite diameter) may serve as the measure of the magnitude of cohesion. Thus, in a tube of 1 mm. diameter, water at 15° rises (the height being corrected for the meniscus) 14.8 mm., and ether at t° to a height $(5.35 - 0.028 t)$ mm. The cohesion of a liquid is lessened by heating, and therefore the capillary heights are also diminished. It has been shown by experiment that this decrement is proportional to the temperature, and hence by the aid of capillary observations we are able to form an idea that at a certain temperature the cohesion may vanish. For ether, according to the above formula, this would occur at 191°. If the cohesion disappears from a liquid it becomes a gas, for cohesion is the only point of difference between these two states. A liquid in evaporating and overcoming the force of cohesion, absorbs heat. Therefore the absolute boiling-point was defined by me (1861) as that temperature at which: (a) a liquid cannot exist as a liquid, but forms a gas which cannot pass into a liquid state under any pressure whatever; (b) its cohesion is zero; and (c) the latent heat of evaporation = 0.

the **liquefaction** of this gas is only possible at low temperatures, and under great pressures.³⁰ This conclusion was verified (1877) by the experiments of Pictet and Cailletet.³¹ They compressed gases at a very

This definition was but little known until Andrews (1869) explained the matter from another aspect by starting from gases. He discovered that carbonic anhydride cannot be liquefied by any degree of compression at temperatures above 31° , whilst at lower temperatures it can be liquefied. He called this temperature the *critical temperature*. It is evident that it is the same as the absolute boiling-point. We shall afterwards designate it by *tc*. At low temperatures a gas which is subjected to a pressure greater than its maximum pressure is transformed into a liquid, which, in evaporating, gives a saturated vapour possessing this maximum pressure; whilst at temperatures above *tc*, the pressure to which the gas is subjected may increase indefinitely. However, under these conditions the volume of the gas does not change indefinitely but approaches a definite limit (see notes 25 and 28)—that is, it resembles in this respect a liquid or a solid which is altered but little in volume by pressure. The volume which a liquid or gas occupies at *tc* is termed the **critical volume**, and corresponds with the **critical pressure**, which we will designate by *pc* and express in atmospheres. It is evident from what has been said that the discrepancies from Mariotte and Boyle's law, the absolute boiling-point, the density in the liquid and compressed gaseous states, and the properties of liquids, must all be intimately connected together. We shall consider these relations in one of the following notes. At present we will supplement the above observations by the values of *tc* and *pc* for certain liquids and gases which have been investigated in this respect—

<i>tc</i>		<i>pc</i>	<i>tc</i>		<i>pc</i>
H ₂	— 240°	15	CH ₃ COOH	+ 322°	57
N ₂	— 146°	33	H ₂ S	+ 108°	92
CO	— 140°	39	C ₂ N ₂	+ 124°	62
O ₂	— 119°	50	NH ₃	+ 131°	114
CH ₄	— 100°	50	CH ₃ Cl	+ 141°	73
NO	— 93°	71	SO ₂	+ 155°	79
C ₂ H ₆	— 40°	50	C ₅ H ₁₀	+ 192°	34
C ₂ H ₄	+ 10°	51	C ₄ H ₁₀ O	+ 194°	36
CO ₂	+ 32°	77	CHCl ₃	+ 268°	55
N ₂ O	+ 39°	78	CS ₂	+ 273°	83
C ₂ H ₂	+ 37°	68	C ₆ H ₆	+ 288°	48
HCl	+ 52°	86	C ₆ H ₅ F	+ 287°	45
H ₂ O	+ 365°	200	C ₆ H ₅ Cl	+ 360°	45
CH ₃ OH	+ 240°	79	C ₆ H ₅ Br	+ 397°	45
C ₂ H ₅ OH	+ 243°	63	C ₆ H ₅ I	+ 448°	45

Young and Guy (1891) showed that *tc* and *pc* clearly depend upon the composition and molecular weight.

³⁰ I came to this conclusion in 1870 (*Ann. Phys. Chem.* **141**, 623).

³¹ **Pictet**, in his researches, effected the direct liquefaction of many gases, which up to that time had not been liquefied. He employed the apparatus used for the manufacture of ice on a large scale, employing the vaporisation of liquid sulphurous anhydride, which may be liquefied by pressure alone. This anhydride is a gas which is transformed into a liquid at the ordinary temperature under a pressure of several atmospheres (see note 27), and boils at -10° at the ordinary atmospheric pressure. The liquid, like all others, boils at a lower temperature under a diminished pressure, and by continually pumping out the gas which comes off by means of a powerful air-pump its boiling-point falls as low as -75° . Consequently if, on the one hand, liquid sulphurous anhydride be forced into a vessel, and on the other hand the gas be pumped from the same vessel by powerful air-pumps, the temperature falls to -75° . If a second vessel is placed inside this one, then another gas may be easily liquefied in it at the low temperature

low temperature, and then allowed them to expand, either by directly decreasing the pressure or by allowing them to escape into the air, by which means the temperature fell still lower, and then, just as steam produced, if the latter is less than its critical temperature. Pictet in this manner easily liquefied carbonic anhydride, CO_2 (at -60° under a pressure of from four to six atmospheres). This gas is more refractory to liquefaction than sulphurous anhydride, but for this reason it gives on evaporating a still lower temperature than can be attained by the evaporation of sulphurous anhydride. A temperature of -80° may be obtained by the evaporation of liquid carbonic anhydride at a pressure of 760 mm., and in an atmosphere rarefied by a powerful pump the temperature falls to -140° . By employing such low temperatures it was possible, with the aid of pressure, to liquefy the majority of the other gases, but not hydrogen. It is evident that special pumps which are capable of rarefying gases are necessary to reduce the pressure in the chambers in which the sulphurous and carbonic anhydrides boil; and that, in order to recondense the resultant gases into liquids, special force pumps are required for pumping the liquid anhydrides into the refrigerating chamber. Thus, in Pictet's apparatus (fig. 25), the

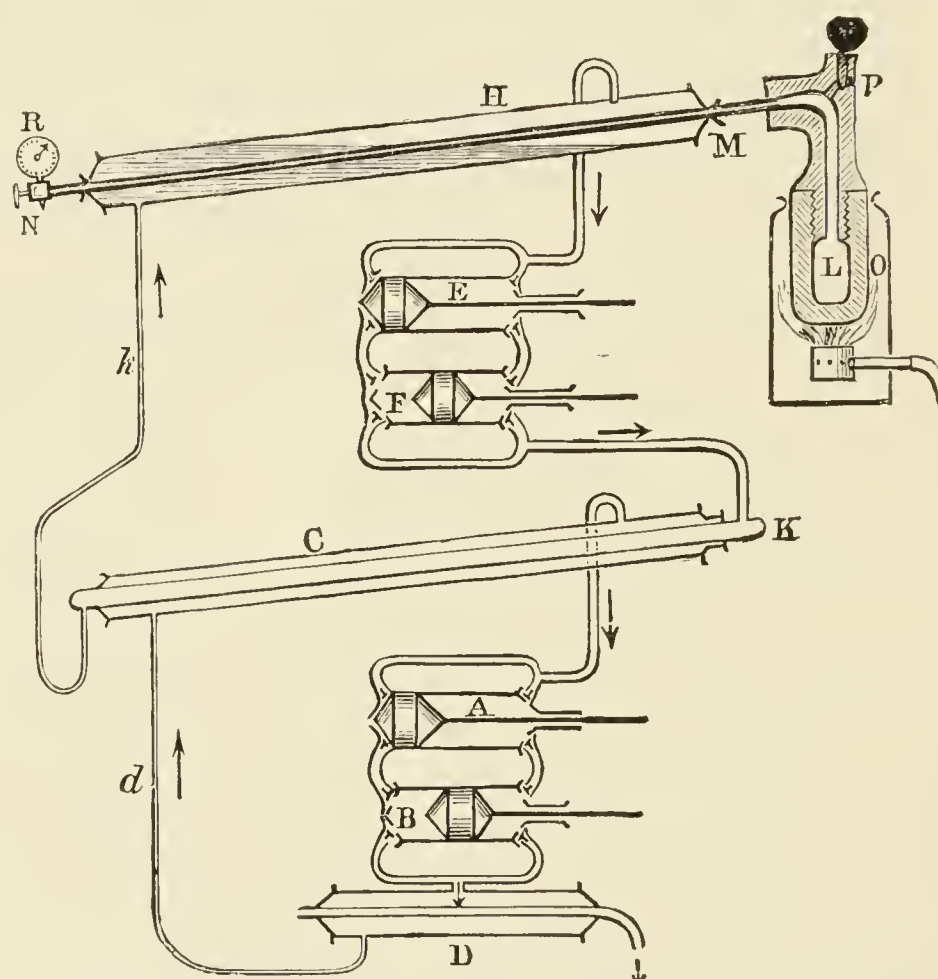


FIG. 25.—General arrangement of the apparatus employed by Pictet for liquefying gases.

carbonic anhydride was liquefied by the aid of the pumps E A F, which compressed the gas (at a pressure of 4–6 atmospheres) and forced it into the tube K, vigorously cooled by being surrounded with boiling liquid sulphurous anhydride, which was condensed in the tube C by the pump B, and rarefied by the pump A. The liquefied carbonic anhydride flowed down the tube K into the tube H, in which it was subjected to a low pressure by the pump E, and thus gave a very low temperature of about -140° . The pump E carried off the vapour of the carbonic anhydride, and conducted it to the pump F, by which it was again liquefied. The carbonic anhydride thus made an entire circuit—that is, it passed from a rarefied vapour of small pressure and low temperature into a compressed and cooled gas, which was transformed into a liquid, which again vaporised and produced a low temperature.

Inside the wide inclined tube H, where the carbonic acid evaporated, was placed a

when rapidly rarefied³² deposits liquid water in the form of a fog, hydrogen in expanding forms a fog, thus indicating its passage into

second and narrow tube, M, containing hydrogen, which was generated in the vessel L by heating a mixture of sodium formate and caustic soda ($\text{CHO}_2\text{Na} + \text{NaHO} = \text{Na}_2\text{CO}_3 + \text{H}_2$). This vessel and the tube M were made of thick copper, and could withstand great pressures. They were, moreover, hermetically connected together and closed up. Thus the gas evolved had no outlet, accumulated in a limited space, and its pressure increased in proportion to the amount of it evolved. This pressure was recorded on a metallic manometer, R, attached to the end of the tube M. As the hydrogen in this tube was submitted to a very low temperature and a powerful pressure, all the necessary conditions were present for its liquefaction. When the temperature had fallen to -140° and the manometer R indicated a pressure of 600 atmospheres in the tube M, this pressure did not apparently rise with a further evolution of hydrogen in the vessel L. Pictet regarded this as an indication that the pressure of the vapour of the hydrogen had attained a maximum corresponding with -140° , and that consequently all the excess of the gas was condensed to a liquid. As a matter of fact Pictet could not possibly have obtained liquid hydrogen, for -140° was far too high a temperature, considering that the critical point of hydrogen lies at about -240° ; but he obtained oxygen, nitrogen, and many other gases in a liquid state, and this was a great novelty in those days.

³² At the same time (1879) as Pictet was working on the liquefaction of gases in Switzerland, **Cailletet**, in Paris, was occupied with the same subject, and his results, although not so convincing as Pictet's, still showed that the majority of gases, previously unliquefied, were capable of passing into a liquid state. Cailletet subjected gases to a pressure of several hundred atmospheres in narrow thick-walled glass tubes (fig. 26) and then cooled the compressed gas as far as possible by surrounding it with a freezing mixture; a cock was then rapidly opened for the outlet of mercury from the tube containing the gas, which consequently rapidly and vigorously expanded. This rapid expansion of the gas would produce great cold, just as the rapid compression of a gas evolves heat and causes a rise in temperature. This cold was produced at the expense of the gas itself, for in rapidly expanding its particles were not able to absorb heat from the walls of the tube, and in cooling a portion of the expanding gas was transformed into liquid. This was seen from the formation of cloud-like drops like a fog which rendered the gas opaque. Thus Cailletet proved the possibility of the liquefaction of gases, but he did not isolate the liquids.

The methods of Pictet and Cailletet were afterwards improved by Olszewski, Wroblewski, Dewar, and others. In order to obtain a still lower temperature they employed, instead of carbonic acid gas, liquid ethylene (C_2H_4) or nitrogen and oxygen, whose evaporation at low pressures produces a much lower temperature (as low as -200°). They also improved on the methods of determining such low temperatures without, however, essentially altering the principle.

The most instructive results have been obtained in recent years by Professor Dewar in the Royal Institution of London, which is glorified by the names of Davy, Faraday, and Tyndall. Dewar, by working with large quantities and powerful pumps, obtained many kilograms of oxygen and air (the boiling-point under the atmospheric pressure = -190°) in a liquid state, and kept them in this state for a length of time by means of open glass vessels (constructed as seen in the drawing)

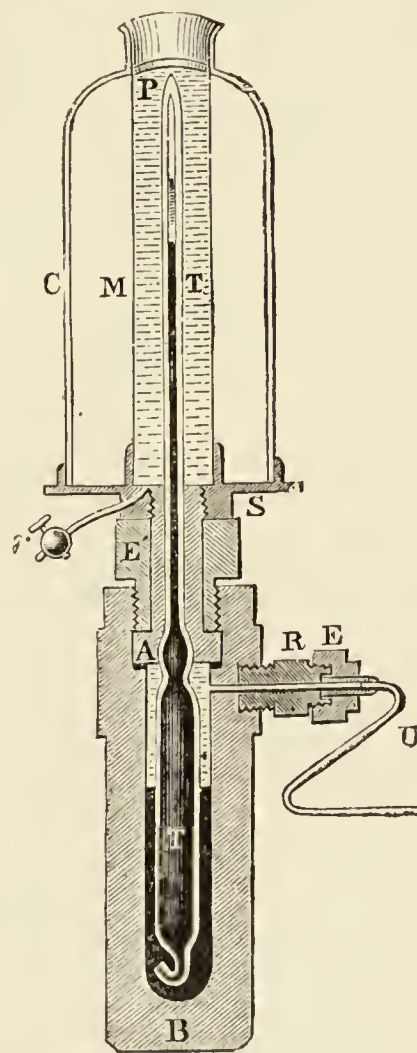


FIG. 26.—Cailletet's apparatus for liquefying gases.

a liquid state. But the first of these experimenters was unable to preserve this liquid, even for a short time, to determine its properties,

with double walls (silvered inside to reflect the rays of heat) having a vacuum between them, which prevented the rapid transference of heat, and so gave the possibility of

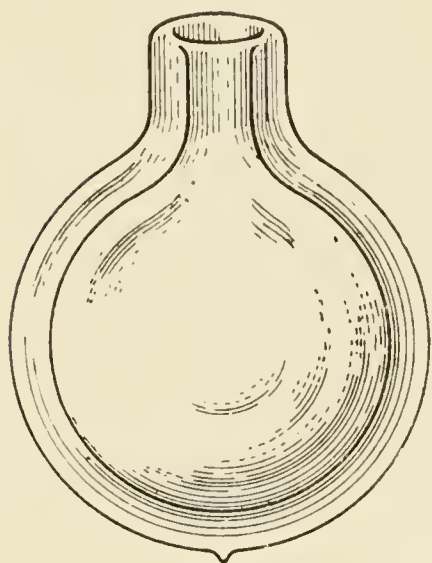


FIG. 27.—Dewar's vacuum-jacketed vessel for liquefied gases.

maintaining very low temperatures inside the vessel for a long period of time. The liquefied oxygen or air can be poured from one vessel into another and used for any investigations. Thus, in June 1894, Professor Dewar showed that at the low temperature produced by liquid oxygen many substances become phosphorescent (self-luminous; for instance, oxygen on passing into a vacuum) and fluoresce (emit light after being illuminated; for instance, paraffin, glue, &c.) much more powerfully than at the ordinary temperature; also that solids then greatly alter in their mechanical properties, &c. The liquid gas poured into the above vessel only remains as such at the ordinary temperature, because it preserves its own low temperature (with air, for instance, this is -191° under the corresponding pressure) and does not evaporate to any extent, because that would require the absorption of heat (so-called latent) which penetrates with difficulty

and but slowly through the double walls, just as the heat of a warm room passes with difficulty through a double window. It was the employment of such vessels with double (and even treble) walls which enabled Dewar (1898) not only to obtain liquid hydrogen

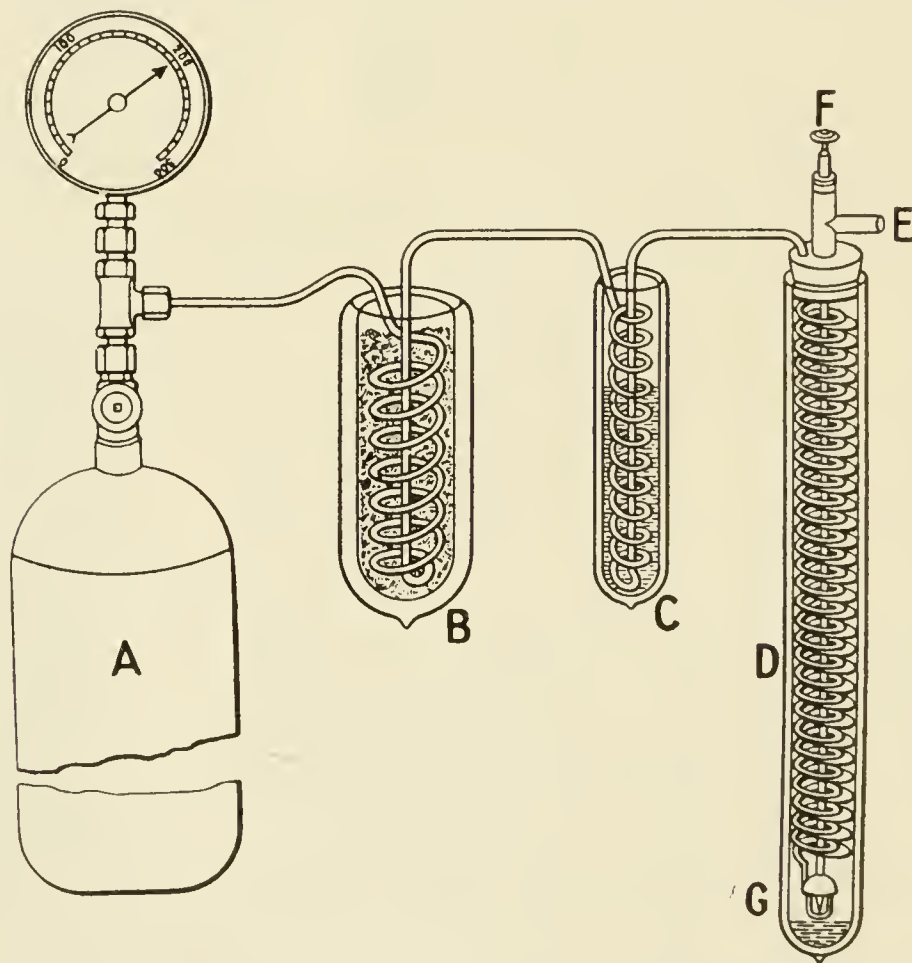


FIG. 28.—Dewar's apparatus for liquefying hydrogen.

but to keep it as such for a sufficient length of time to determine its properties and even its transition into a solid state. A scheme of the apparatus, used by Dewar for this purpose, is given in the accompanying drawings. *A* is a metallic reservoir con-

notwithstanding the employment of a temperature of -200° and a pressure of 200 atmospheres,³³ although by these means the gases of the atmosphere may be easily liquefied. This is due to the fact that the absolute boiling-point of hydrogen lies lower than that of all other known gases, a fact which also depends on the extreme lightness of hydrogen.³⁴

taining hydrogen under a pressure of 180–200 atmospheres, *B* and *C* are double-walled vessels, with a vacuum between the walls, in which liquid carbonic anhydride and air are evaporated under a diminished pressure and cool the hydrogen passing through the spiral tube to -203° . In the third double-walled vessel, *D*, the refrigerated and liquefied hydrogen expands on opening the cock *F*, which causes its temperature to fall yet further, and it is then obtained as a colourless liquid whose chief properties are given in the text.

³³ The investigations of S. Wroblewski in Cracow clearly show that Pictet could not have obtained liquid hydrogen in the interior of his apparatus, and that if he did obtain it, it could only have been at the moment of its exit due to the fall in temperature following its sudden expansion, as hydrogen is not liquefied by any pressure at -140° because its critical temperature (absolute boiling-point) lies much lower—at about -240° . However, on expansion a fog is formed and a liquid state attained, but the liquid does not separate.

³⁴ After the idea of the absolute temperature of ebullition (*tc*, note 29) had been worked out (about 1870), and its connection with the deviations from Mariotte's law had become evident, and especially after the liquefaction of permanent gases, general attention was turned to the development of the fundamental conceptions of the gaseous and liquid states of matter. Some investigators directed their energies to the further study of vapours (for instance, Ramsay and Young), gases (Amagat), and liquids (Zaencheffsky, Nadeschdin, and others), especially to liquids near the critical temperature and pressure; others (Konovaloff and De Heen) endeavoured to discover the relation between liquids under ordinary conditions (far removed from the critical temperature and pressure) and gases; whilst a third class of investigators (van der Waals, Clausius, and others), starting from the generally accepted principles of the mechanical theory of heat and the kinetic theory of gases, and assuming in gases the existence of those forces which certainly act in liquids, deduced the connection between the properties of one and the other. It would be out of place in an elementary handbook (see Physical Chemistry) like the present to enunciate the whole mass of conclusions arrived at by this method; but it is well to give an idea of the results of van der Waals's considerations, for they explain the gradual uninterrupted passage from a liquid into a gaseous state in the simplest manner, and, although the deduction cannot be considered as complete and decisive (see note 25), nevertheless it penetrates so deeply into the essence of the matter that its signification is not only reflected in a great number of physical investigations, but also in the province of chemistry, where instances of the passage of substances from a gaseous to a liquid state (and conversely) are so common, and where the very processes of dissociation, decomposition, and combination must be identified with a change of physical state of the participating substances, which has been elaborated by Gibbs, Liveing, and others.

For a *given quantity* (weight, mass) of a *definite substance*, its state is expressed by three variables—volume *v*, pressure (elasticity, tension) *p*, and temperature *t*.

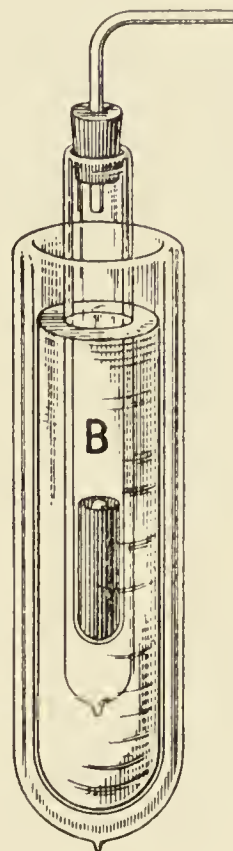


FIG. 29.—Dewar's apparatus for solidifying hydrogen. The inner vacuum vessel, *B*, contains liquid hydrogen, and the outer one liquid air. By pumping gas out of both of these vessels, the temperature of the hydrogen falls to -256° , when it solidifies.

Dewar, who obtained and investigated liquid hydrogen in 1898, showed that the critical temperature of this gas lies at about -240° ,

Although the compressibility—[i.e., $d(v)/d(p)$ —of liquids is small, still it is clearly expressed, and varies not only with the nature of the liquids, but also with their pressure and temperature (the compressibility of liquids at a low temperature is very considerable; for instance, for hydrogen 0.024, nitrogen 0.0056, and oxygen 0.0046). Although, according to Mariotte's law, with small variations of pressure, gases are uniformly compressed, nevertheless the dependence of their volume v on t and p is very complex. This also applies to the coefficient of expansion [$=d(v)/d(t)$, or $d(p)/d(t)$], which also varies with t and p , both for gases (see note 26) and for liquids (at tc it is very considerable, and often exceeds that of gases, 0.00367). Hence, the **equation of condition** must include three variables, v , p , and t . For a so-called perfect (ideal) gas or for inconsiderable variations of density, the elementary expression, $pv = R(273 + t)$ should be accepted, where R is a constant varying with the mass and nature of a gas. In its simplest form the equation may be expressed thus:

$$pv = RT :$$

where T denotes what is termed the absolute temperature, or the ordinary temperature $+273$, that is, $T = t + 273$.

Starting from the supposition of the existence of an attraction or internal pressure (expressed by a) proportional to the square of the density (or inversely proportional to the square of the volume) and of the existence of a real volume or diminished length of path (expressed by b) for each gaseous molecule, **van der Waals** gives for gases the following complex **equation** of condition:—

$$\left(p + \frac{a}{v^2}\right)(v - b) = 1 + 0.00367t,$$

if at 0° and under a pressure $p = 1$ (for example, under the atmospheric pressure), the volume (for instance, a litre) of a gas or vapour be taken as 1, and v and b be therefore expressed by the same units as p and a . The above equation **expresses the deviations** from the laws both of Mariotte and Gay-Lussac. Thus, for hydrogen a must be taken as infinitely small, and $b = 0.0009$, judging by the data for 1,000 and 2,500 metres pressure (note 28). For other permanent gases these deviations may be expressed by giving definite magnitudes of a and b (although van der Waals's formula is not applicable in the case of very small pressures) with sufficient accuracy for present requirements. It is evident that van der Waals's equation can also express the variation of the coefficients of expansion of gases with change either of pressure or of the method of determination (note 26). Besides this, van der Waals's formula shows that the absolute boiling-point $(tc) = 273 \left(\frac{8a}{27b} - 1 \right)$. This is found from the fact that all three possible volumes (the three roots of van der Waals's cubic equation) are then similar and equal, i.e. $(vc) = 3b$. The pressure in this case is given by $(pc) = \frac{a}{27b^2}$. These ratios between the constants a and b and the conditions of the critical state, i.e. (tc) and (pc) , give the possibility of determining one pair of these magnitudes from the others. Thus for ether (note 29), $(tc) = 193^{\circ}$, $(tp) = 40$; hence $a = 0.0307$, $b = 0.00533$, and $(vc) = 0.016$. That mass of ether which at a pressure of one atmosphere at 0° occupies one volume—for instance, a litre—occupies, according to the above-mentioned condition, this critical volume. And as the density of the vapour of ether compared with that of hydrogen is 37, and a litre of hydrogen at 0° and under the atmospheric pressure weighs 0.0896 gram, then a litre of ether vapour weighs 3.32 grams; therefore in a critical state (at 193° and 40 atmospheres) 3.32 grams occupy 0.016 litre, or 16 c.c.; so that 1 gram occupies a volume of about 5 c.c., and the weight of 1 c.c. of ether will then be 0.21. According to the investigations of Ramsay and Young (1887), the critical volume of ether is approximately such at about the absolute boiling-point; but the compressibility of the liquid is so great that the slightest change of pressure or temperature has a considerable effect on the volume.

i.e., at a temperature difficult to attain even by evaporating other liquefied gases under diminished pressure. Dewar succeeded in liquefying hydrogen by cooling it to -220° (which he obtained in liquid oxygen under diminished pressure) under a pressure of 200 atmospheres, and then making it expand rapidly (by letting it flow from an orifice in the vessel holding it) when its temperature fell to -252° , at which temperature liquid hydrogen boils under the ordinary pressure (about 760 mm.) Liquid hydrogen then occurs as a colourless liquid, a litre of which weighs about 0.086 gram at its melting-point, -256° (it is thus the lightest liquid known), and which freezes (on lowering the

But the investigations of the above savants gave another indirect demonstration of the truth of van der Waals's equation. They also found for ether that the isochords, or the lines of equal volumes (if both t and p vary), are generally straight lines, which is a direct result of van der Waals's formula.

When, in 1883, I demonstrated that the specific gravity of liquids decreases *approximately* in proportion to the rise of temperature [$S = S_0 - Kt$ or $S_t = S_0 (1 - kt)$], where k is the modulus of expansion, which varies with the nature of the liquid, then, in general, not only does a connection arise between gases and liquids with respect to a change of volume, but also it would appear possible, by applying van der Waals's formula, to judge, from the phenomena of the expansion of liquids, as to their transition into vapour, and to connect together all the principal properties of liquids, which up to this time had not been considered to be in direct dependence. Thus Thorpe and Rücker found that $2(tc) + 273 = 1/k$, where k is the *modulus* of expansion in the above-mentioned formula. For example, the expansion of ether is expressed with sufficient accuracy from 0° to 100° by the equation: $S_t = 0.736 (1 - 0.00154t)$, or $V_t = 1/(1 - 0.00154t)$, where 0.00154 is the modulus of expansion, so that $(tc) = 188^{\circ}$, direct observation giving 194° . For silicon tetrachloride, SiCl_4 , the modulus equals 0.00136, whence $(tc) = 231^{\circ}$, the experimental value being 230° . On the other hand, D. P. Konovaloff, admitting that the external pressure, p , in liquids is insignificant when compared with the internal (a in van der Waals's formula), and that the work in the expansion of liquids is proportional to their temperature (as in gases), deduced directly from van der Waals's equation, the above-mentioned formula for the expansion of liquids, and also the magnitudes of the latent heat of evaporation, of the cohesion, and of the compressibility. In this way van der Waals's formula embraces the gaseous, critical, and **liquid states** of substances, and shows the connection between them. On this account, although van der Waals's formula cannot be considered as perfectly general and accurate, yet it is not only very much more exact than $pv = RT$, but it is also more comprehensive, because it applies both to gases and liquids. Further research will naturally give a closer proximity to truth, and will show the connection between composition and the constants (a and b); but this form of the equation of state marks great scientific progress.

Clausius (in 1880), taking into consideration the variability of a in van der Waals's formula with the temperature, gave the following equation of condition:—

$$\left(p + \frac{a}{T(v+c)^2}\right)(v-b) = RT.$$

Sarrau (1882) applied this formula to Amagat's data for hydrogen, and found $a = 0.0551$, $c = -0.00043$, $b = 0.00089$, and therefore calculated its absolute boiling-point to be -174° , and $(pc) = 99$ atmospheres. But as similar calculations for oxygen (-105°), nitrogen (-124°), and marsh gas (-76°) gave tc higher than it really is, the absolute boiling-point of hydrogen must lie below -174° , and as a matter of fact it is about -240° . Further details on the subjects here touched upon must be sought in physical chemistry.

pressure and temperature) into colourless crystals, melting at about -256° .

Although a substance which passes with great difficulty into a liquid or solid state by the action of physico-mechanical forces, hydrogen loses its gaseous state (that is, its elasticity, or the physical energy of its molecules, or their rapid progressive motion) with comparative ease under the influence of chemical attraction,³⁵ as is seen, not only from the fact that hydrogen and oxygen (two permanent gases) form liquid water, but also from many phenomena of the absorption of hydrogen.

Hydrogen is vigorously absorbed by certain solids; for example, by charcoal and by spongy platinum. If a piece of freshly ignited charcoal be introduced into a cylinder full of hydrogen standing in a mercury bath, the charcoal will absorb as much as twice its volume of hydrogen. Spongy platinum condenses still more hydrogen. But **palladium**, a grey metal which is found with platinum, **absorbs** more **hydrogen** than any other metal. Graham showed that, when heated to a red heat and cooled in an atmosphere of hydrogen, palladium retains as much as 600 volumes of the gas. When once absorbed, the hydrogen is retained at the ordinary temperature, and is only given up at a red heat.³⁶ This capacity of certain metals for the absorption of hydrogen explains the property of hydrogen of passing through metallic tubes made, for instance, of iron or platinum.³⁷ This property is termed

³⁵ This and a number of similar cases clearly show how great are internal chemical forces compared with physical and mechanical forces.

³⁶ The property of palladium of absorbing hydrogen, and of increasing in volume in so doing, may be easily demonstrated by taking a sheet of palladium, varnished on one side, and using it as a cathode. The hydrogen which is evolved by the action of the current is retained by the unvarnished surface, as a consequence of which the sheet curls up. By attaching a pointer (for instance, a quill) to the end of the sheet, this bending effect is rendered strikingly evident, and on reversing the current (when oxygen will be evolved and will combine with the absorbed hydrogen, forming water) it may be shown that on losing the hydrogen the palladium regains its original form.

³⁷ Deville discovered that iron and platinum become pervious to hydrogen at a red heat. He speaks of this in the following terms:—‘The permeability of such homogeneous substances as platinum and iron is quite different from the passage of gases through such non-compact substances as clay and graphite. The permeability of metals depends on their expansion, brought about by heat, and proves that metals and alloys have a certain porosity.’ However, Graham proved that it is only hydrogen which is capable of passing through the above-named metals in this manner. Oxygen, nitrogen, ammonia, and many other gases only pass through in extremely minute quantities. Graham showed that at a red heat about 500 c.c. of hydrogen per minute pass through a surface of one square metre of platinum 1.1 mm. thick, but that with other gases the amount transmitted is hardly perceptible. Indiarubber has the same capacity for allowing the transference of hydrogen through its substance (see Chapter III.), and at the ordinary temperature one square metre, 0.014 mm. thick, transmits about 127 c.c. of hydrogen per minute. In the experiment on the decomposition of water by heat in porous tubes the clay tube may be exchanged for a platinum one with advantage. Graham showed that by placing a platinum tube containing hydrogen under these conditions, and surrounding

occlusion, and is very similar to solution: it is based on the capacity of metals of forming with hydrogen unstable, easily dissociating compounds,³⁸ similar to those which salts form with water. Some of these direct compounds of hydrogen with metals have been isolated by Winkler, Moissan, and others (see Chaps. XII., XIV. &c.).

At the ordinary temperature hydrogen enters very rarely and feebly into chemical reaction. The capacity of gaseous **hydrogen** for reaction becomes evident only under a change of circumstances—by compression, heating, or the action of light, or at the moment of its evolution. However, even under these circumstances it **combines** directly with only a very few of the elements. Hydrogen combines directly with oxygen, sulphur, fluorine, carbon, potassium, and certain other elements, but not with the majority of the metals, nor with nitrogen, phosphorus, &c. Compounds of hydrogen with certain elements on which it does not act directly are, however, known, and are obtained by reactions of decomposition, or of double decomposition, of other hydrogen compounds. The property possessed by hydrogen of combining with oxygen at a red heat determines its combustibility. We have already seen that hydrogen easily takes fire, and that it then burns with a pale—that is, non-luminous—flame.³⁹ Hydrogen does not combine with the oxygen of the atmosphere at the ordinary temperature; but this combination takes place at a red heat,⁴⁰ and is accompanied by the evolution of

it by a tube containing air, the transference of the hydrogen may be observed by the decrease of pressure in the platinum tube. In one hour almost all the hydrogen (97 per cent.) had passed from the tube, without being replaced by air. It is evident that the occlusion and passage of hydrogen through metals capable of occluding it are not only intimately connected together, but are dependent on the capacity of metals to form compounds of various degrees of stability with hydrogen-like solutions.

³⁸ It appeared on further investigation that palladium gives a definite compound, Pd_2H (see Chapter XXIII.), with hydrogen; but what was most instructive was the investigation of sodium hydride, Na_2H .

Molten iron absorbs hydrogen, but in solidifying it expels it. The solution of hydrogen by metals is to a certain degree based on its affinity for metals, and must be likened to the solution of metals in mercury and to the formation of alloys. In its chemical properties hydrogen, as we shall see later, has much of a metallic character. The metallic properties of hydrogen are also evinced in the fact that it is a good conductor of heat, which is not the case with other gases (Magnus).

³⁹ If it be desired to obtain a perfectly colourless hydrogen flame, the gas must issue from a platinum nozzle, as the glass end of a gas-conducting tube imparts a yellow tint to the flame, owing to the presence of sodium in the glass.

⁴⁰ Let us imagine that a stream of hydrogen passes along a tube, and let us mentally divide this stream into several parts, consecutively passing out from the orifice of the tube. The first part is lighted—that is, brought to a state of incandescence, in which state it combines with the oxygen of the atmosphere. A considerable amount of heat is evolved in the combination. The heat evolved then ignites the second part of hydrogen coming from the tube, and, therefore, when once ignited, the hydrogen continues to burn, if there is a continual supply of it, and if the atmosphere in which it burns is unlimited and contains oxygen.

much heat. The product of this combination is water—that is, a compound of oxygen and hydrogen. This is the **synthesis of water**, and we have already noticed its analysis or decomposition into its component parts. The synthesis of water may be very easily observed if a cold glass bell jar be placed over a burning hydrogen flame, or, better still, if the hydrogen flame be lighted in the tube of a condenser. The water will condense in drops, as it is formed, on the walls of the condenser and trickle down.⁴¹

Light does not aid the combination of hydrogen and oxygen, so that a mixture of these two gases does not change when exposed to the action of light; but an electric spark acts just like a flame, and this is taken advantage of for inflaming a mixture of oxygen and hydrogen, or detonating gas, inside a vessel, as will be explained in the following chapters. As hydrogen (and oxygen also) is condensed by spongy platinum, with rise of temperature, and as platinum acts by contact (Introduction), therefore hydrogen also combines with oxygen, under the influence of platinum, as was shown by Döbereiner. If spongy platinum is thrown into a mixture of hydrogen and oxygen, an explosion takes place; and if a mixture of the gases be passed over spongy platinum, combination will also ensue, and the platinum become red-hot.⁴² Hydrogen exhibits

⁴¹ The combustibility of hydrogen may be shown by the direct decomposition of water by sodium. If a pellet of sodium is thrown into a vessel containing water, it floats on the water and evolves hydrogen, which may be lighted. The presence of sodium imparts a yellow tint to the flame. If potassium be taken, the hydrogen bursts into flame spontaneously, because sufficient heat is evolved in the reaction to ignite the hydrogen. The flame is coloured violet by the potassium. If sodium be thrown, not on to water, but on to an acid, it will evolve more heat, and the hydrogen will then also burst into flame. These experiments must be carried on with caution, as, sometimes towards the end, a mass of sodium oxide (note 8) is produced, and flies about. It is therefore best to cover the vessel in which the experiment is carried on.

⁴² This property of spongy platinum is made use of in the so-called hydrogen cigar-lighter. It consists of a glass cylinder or beaker, inside which there is a small lead stand (which is not acted on by sulphuric acid), on which a piece of zinc is laid. This zinc is covered by a bell, which is open at the bottom and furnished with a cock at the top. Sulphuric acid is poured into the space between the bell and the sides of the outer glass cylinder, and will thus compress the gas in the bell. If the cock of the cylinder be opened the gas will escape by it, and will be replaced by the acid, which, coming into contact with the zinc, evolves hydrogen, and this will escape through the cock. If the cock be closed, then the hydrogen evolved will increase the pressure of the gas in the bell, and thus again force the acid into the space between the bell and the walls of the outer cylinder. Thus the action of the acid on the zinc may be stopped or started at will by opening or shutting the cock, and consequently a stream of hydrogen may be turned on at any time. Now, if a piece of spongy platinum be placed in this stream, the hydrogen will take fire, because the spongy platinum becomes hot in condensing the hydrogen and inflames it. The considerable rise in temperature of the platinum depends, among other things, on the fact that the hydrogen condensed in its pores comes into contact with previously absorbed and condensed atmospheric oxygen, with which hydrogen combines with great facility in this form. In this manner the hydrogen cigar-lighter gives a stream of burning hydrogen when the cock is open. In order that it should work

its greatest affinity for direct reaction, with fluorine and chlorine, forming hydrofluoric, HF, and hydrochloric acids, HCl, which will be considered more fully in Chapter XI.

Although gaseous hydrogen does not act directly ⁴³ on many substances, yet in a **nascent state** reaction often takes place. Thus, for instance, water on which sodium amalgam is acting contains hydrogen in a nascent state. The hydrogen is here evolved from a liquid, and at the first moment of its formation must be in a condensed state.⁴⁴ In this condition it is capable of reacting on substances on which it does not act in a gaseous state. Reactions of substitution or **displacement of metals by hydrogen** at the moment of its formation are particularly numerous.⁴⁵

regularly it is necessary that the spongy platinum should be quite clean, and it is best enveloped in a thin sheet of platinum foil, which protects it from dust. In any case, after some time it will be necessary to clean the platinum, and this may be easily done by boiling it in nitric acid, which does not dissolve the platinum, but frees it from all dirt. This imperfection has given rise to several other forms, in which an electric spark is made to pass in front of the orifice from which the hydrogen escapes. This is arranged in such a manner that the zinc of a galvanic element is immersed when the cock is turned, or a small coil giving a spark is put into circuit on turning the hydrogen on.

⁴³ Under conditions similar to those in which hydrogen combines with oxygen it is also capable of combining with chlorine. A mixture of hydrogen and chlorine explodes on the passage of an electric spark through it, or on contact with an incandescent substance, or in the presence of spongy platinum; but, besides this, the action of light alone is enough to bring about the combination of hydrogen and chlorine. If a mixture of equal volumes of hydrogen and chlorine is exposed to the action of sunlight, complete combination rapidly ensues, accompanied by a report. Hydrogen does not combine directly with carbon, either at the ordinary temperature or under the action of heat and pressure. But if an electric current be passed through carbon electrodes at a short distance from each other (as in the electric light or voltaic arc), so as to form an electric arc in which the particles of carbon are carried from one pole to the other, then, in the intense heat to which the carbon is subjected in this case, it is capable of combining with hydrogen. A gas of peculiar smell called acetylene, C_2H_2 , is thus formed from carbon and hydrogen.

⁴⁴ There is another explanation of the facility with which hydrogen reacts in a nascent state. We shall afterwards learn that the molecule of hydrogen contains two atoms, H_2 , but there are elements the molecules of which contain only one atom—for instance, mercury. Therefore every reaction of gaseous hydrogen must be accompanied by the disruption of that bond which exists between the atoms forming a molecule. At the moment of evolution, however, it is supposed that free atoms exist, and in this condition, according to the hypothesis, act energetically. This hypothesis is not based upon facts, and the idea that hydrogen is condensed at the moment of its evolution is more natural, and is in accordance with the fact (note 12) that compressed hydrogen displaces palladium and silver (Brunner, Beketoff)—that is, acts as at the moment of its liberation. It is impossible at present to form any idea of the properties of the isolated atoms (ions) of hydrogen, for certain of the elements whose molecules contain one atom are chemically very active (for instance, Na) while others (such as argon) are perfectly inert.

⁴⁵ When, for instance, an acid and zinc are added to a salt of silver, the silver is reduced; but this may be explained as a reaction of the zinc, and not of the hydrogen at the moment of its formation. There are, however, examples to which this explanation is entirely inapplicable; thus, for instance, hydrogen, at the moment of its liberation,

Metals, as we shall afterwards see, are in many cases able to replace each other; they also, and in some cases still more easily, replace and are replaced by hydrogen. We have already seen examples of this in the formation of hydrogen from water, sulphuric acid, &c. In all these cases the metal sodium, iron, or zinc displaces the hydrogen which occurs in these compounds. Hydrogen may be displaced by metals from many of its compounds in exactly the same manner as it is displaced from water; thus, for example, hydrochloric acid, which is formed directly by the combination of hydrogen with chlorine, gives hydrogen by the action of a great many metals, just as sulphuric acid does. Potassium and sodium also displace hydrogen from its compounds with nitrogen; it is only from its compounds with carbon that hydrogen is not displaced by metals. Hydrogen, in its turn, is able to replace metals: this is accomplished most easily on heating, and with those metals which do not themselves displace hydrogen. If hydrogen be passed over the compounds of many metals with oxygen maintained at a red heat, it takes up the oxygen from the metals and displaces them just as it is itself displaced by metals. If hydrogen is passed over the compound of oxygen with copper at a red heat, then metallic copper and water are obtained— $\text{CuO} + \text{H}_2 = \text{H}_2\text{O} + \text{Cu}$. This kind of double decomposition is called **reduction**, with reference to the metal, which is thus reduced to a metallic state from its combination with oxygen. But it must be recollected that all metals do not displace hydrogen directly from its compound with oxygen; and, conversely, hydrogen is not able to displace all metals from their compounds with oxygen, &c.; thus it does not displace potassium, calcium, or aluminium from its compounds with oxygen. If the metals be arranged in the following series: K, Na, Ca, Al . . . Fe, Zn, H . . . Cu, Pb, Ag, Au, then the first are able to take up oxygen from water—that is, displace hydrogen—whilst the last do not act thus, but are, on the contrary, reduced by hydrogen—that is, have, as is said, a less affinity for oxygen than hydrogen, whilst potassium, sodium, and calcium have more. This is also expressed by the amount of heat evolved in the act of combination with oxygen (see note 7), and is shown by the fact that potassium and sodium and other similar metals evolve heat in decomposing water; but copper, easily takes up oxygen from its compounds with nitrogen if they be in solution, and converts the nitrogen into its hydrogen compound. Here the nitrogen and hydrogen, so to speak, meet at the moment of their liberation, and in this state combine.

It is evident from this that the elastic gaseous state of hydrogen fixes the limit of its energy and prevents it from entering into those combinations of which it is capable. In the nascent state we have hydrogen which is not in a gaseous state, and its action is then much more energetic. At the moment of evolution that heat which would be latent in the gaseous hydrogen is transmitted to its molecules, and consequently they are in a state of strain, and hence capable of acting on many substances.

silver, and the like do not do this, because in combining with oxygen they evolve less heat than hydrogen does, and therefore it happens that when hydrogen reduces these metals heat is evolved. Thus, for example, if 16 grams of oxygen combine with copper, 38,000 units of heat are evolved; and when 16 grams of oxygen combine with hydrogen, forming water, 69,000 units of heat are evolved; whilst 23 grams of sodium, in combining with 16 grams of oxygen, evolve 100,000 units of heat. This example clearly shows that chemical reactions which proceed directly and unaided evolve heat. Sodium decomposes water, and hydrogen reduces copper, because they are **exothermal** reactions, or such as evolve heat; copper does not decompose water, because such a reaction would be accompanied by an absorption (or secretion) of heat, or belongs to the class of **endothermal** reactions in which heat is absorbed; and such reactions do not generally proceed directly, although they may take place with the aid of energy (electrical, thermal, &c.) borrowed from some foreign source.⁴⁶

The reduction of metals by hydrogen is taken advantage of for **determining the composition of water by weight**. Copper oxide is usually chosen for this purpose. It is heated to redness in hydrogen, and the quantity of water thus formed is determined, while the quantity of oxygen which occurs in it is found from the loss of weight of the copper oxide. The copper oxide must be weighed immediately before and after the experiment. The difference shows the weight of the oxygen which entered into the composition of the water formed. In this manner only solids have to be weighed, which is a very great gain in the accuracy of the results obtained.⁴⁷ Dulong and Berzelius (1819) were the first to determine the composition of water by this method, and they found that water contains 88·91 parts of oxygen and 11·09 of hydrogen in 100 parts by weight, or 8·008 parts of oxygen per one part of hydrogen. Dumas (1842) improved on this method,⁴⁸ and found that

⁴⁶ Several numerical data and ideas bearing on this matter are given in notes 7, 9, and 11. It must be observed that the action of iron or zinc on water is reversible. But the reaction $\text{CuO} + \text{H}_2 = \text{Cu} + \text{H}_2\text{O}$ is not reversible; the difference between the degrees of affinity is very great in this case, and, therefore, so far as is at present known, no hydrogen is liberated even in the presence of a large excess of water. If definite amounts of a metal and acid be taken and their reaction be carried on in a closed space, the evolution of hydrogen will cease when its pressure equals that at which compressed hydrogen displaces the metal. The result depends upon the nature of the metal and the strength of the solution of acid. Tammann and Nernst (1892) found that the metals stand in the following order in respect to this limiting pressure of hydrogen:—Na, Mg, Zn, Al, Cd, Fe, Ni.

⁴⁷ This determination may be carried on in an apparatus like that mentioned in note 13 of Chapter I.

⁴⁸ We will proceed to describe Dumas's method and results. For this determination, pure and dry copper oxide is necessary. In each determination Dumas took a sufficient

water contains 12.575 parts of hydrogen per 100 parts of oxygen—that is, 7.990 parts of oxygen per 1 part of hydrogen—and it is therefore

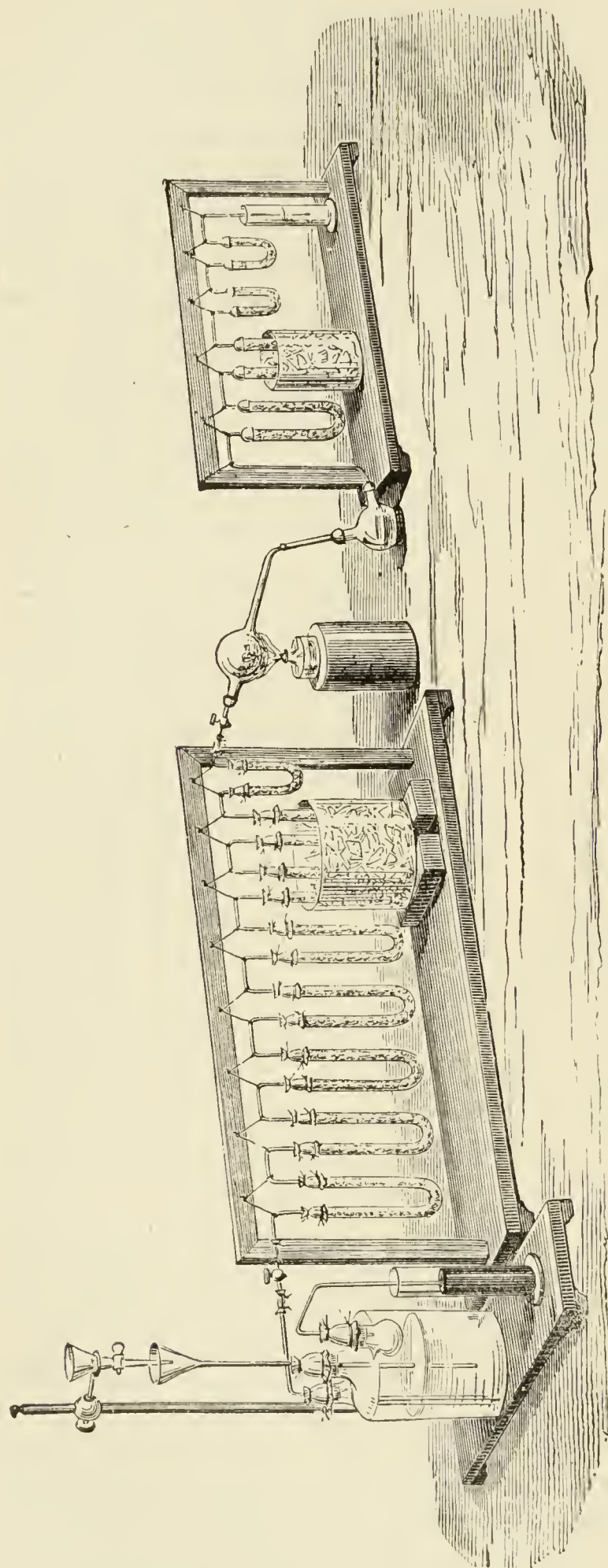


FIG. 30.—Apparatus employed by Dumas for determining the composition of water. Described in text.

quantity of copper oxide for the formation of 50 grams of water. As the oxide of copper was weighed before and after the experiment, and as the amount of oxygen contained in water was determined by the difference between these weights, it was essential that no other substance besides the oxygen forming the water should be evolved from the oxide of copper during its ignition in hydrogen. It was necessary also that the hydrogen should be perfectly pure, and free not only from traces of moisture, but from any other impurities which might dissolve in the water or combine with the copper and form some other compound with it. The bulb containing the oxide of copper (fig. 30), which was heated to redness, should be quite free from air, as otherwise the oxygen in the air might, in combining with the hydrogen passing through the vessel, form water in addition to that formed by the oxygen of the oxide of copper. The water formed should be entirely absorbed in order to accurately determine its quantity. The hydrogen was evolved in a three-necked bottle. The sulphuric acid, for acting on the zinc, is poured through funnels into the middle neck. The hydrogen evolved in the Woulfe's bottle passes through U-tubes, in which it is purified, to the bulb, where it comes into contact with the incandescent copper oxide, forms water, and reduces the oxide to metallic

copper; the water formed is condensed in the second bulb, and any passing off is absorbed in the second set of U-tubes. This is the general arrangement of the apparatus. The loss in weight of the bulb containing the copper oxide shows the

accepted that *water contains eight parts by weight of oxygen to one part by weight of hydrogen*. And as the most exact determinations

quantity of oxygen which entered into the composition of the water formed, the weight of the latter being shown by the gain in weight of the absorbing apparatus. Knowing the amount of oxygen in the water formed, we also know the quantity of hydrogen contained in it, and consequently we can determine the composition of water by weight. This is the essence of the determination. We will now turn to certain details. In one neck of the three-necked bottle a tube is placed dipping under mercury. This serves as a safety-valve to prevent the pressure inside the apparatus becoming too great owing to the rapid evolution of hydrogen. If the pressure rose to any considerable extent, the current of gases and vapours would be very rapid, and, as a consequence, the hydrogen would not be perfectly purified nor the water entirely absorbed in the tubes placed for this purpose. In the third neck of the Woulfe's bottle is a tube conducting the hydrogen to the purifying apparatus, consisting of eight U-tubes, destined for the purification and testing of the hydrogen. The hydrogen, evolved from zinc and sulphuric acid, is purified by passing it first through a tube full of pieces of glass moistened with a solution of lead nitrate and then through silver sulphate; the lead nitrate retains sulphuretted hydrogen, while arseniuretted hydrogen is retained by the silver sulphate tube. Caustic potash in the next U-tube retains any acid which might come over. The two following tubes are filled with lumps of dry caustic potash in order to absorb any carbonic anhydride and moisture which the hydrogen might contain. The next two tubes, to remove the last traces of moisture, are filled with phosphoric anhydride, mixed with lumps of pumice-stone. They are immersed in a freezing mixture. The small U-tube contains hygroscopic substances, and is weighed before the experiment: it is used in order to ascertain whether the hydrogen passing through still retains any moisture. If it does not, then the weight of this tube will not vary during the whole experiment, but if the hydrogen evolved still retains moisture, the tube will increase in weight. The copper oxide is placed in the bulb, which, previous to the experiment, is dried with the copper oxide for a long time. The air is then exhausted from it in order to weigh the oxide of copper in a vacuum, and so avoid the need of a correction for weighing in air. The bulb is made of infusible glass, that it may be able to withstand a lengthy (20 hours) exposure to a red heat without changing in form. The weighed bulb is only connected with the purifying apparatus after the hydrogen has passed through for a long time, and after experiment has shown that the hydrogen passing from the purifying apparatus is pure and does not contain any air. The first U-tube contains pieces of ignited potash, and the second and third tubes, phosphoric anhydride or pumice-stone moistened with sulphuric acid. The last tube is employed for determining whether all the moisture is absorbed, and is therefore weighed separately. The glass cylinder contains sulphuric acid, through which the excess of hydrogen passes: it enables the rate at which the hydrogen is evolved to be seen, and shows whether its amount should be decreased or increased.

When the apparatus is fitted up it must be seen that all its parts are hermetically tight before commencing the experiment. When the previously weighed parts are connected together, and the whole apparatus put into communication, the bulb containing the copper oxide is heated with a spirit or other lamp, and the reduction of the copper oxide then takes place, and water is formed. When nearly all the copper oxide is reduced the lamp is removed and the apparatus allowed to cool, the current of hydrogen being kept up all the time. When cool, the drawn-out end of the bulb is fused up, and the hydrogen remaining in it exhausted, in order that the copper may be again weighed in a vacuum. The absorbing apparatus remains full of hydrogen, and would therefore present a less weight than if it were full of air, as it was before the experiment; and for this reason, having disconnected the copper oxide bulb, a current of dry air is passed through it until the gas passing from the glass cylinder is quite free from hydrogen. The condensing bulb and the two tubes next to it are then weighed in order to determine the quantity of water formed. Dumas repeated this experiment

of the composition of water in recent times (Keiser 1888, Morley 1895, Thomsen 1896, &c.) concur in showing that it contains not more than 7,945, and not less than 7,935 parts of oxygen per 1 part by weight of hydrogen, the mean of these, or 7,940 parts of oxygen per 1 part by weight of hydrogen, or, what is almost the same, 8 parts of oxygen per 1.0076 parts of hydrogen, is now adopted wherever great accuracy is required. This corresponds with 88.81 parts of oxygen and 11.19 parts of hydrogen per 100 parts of water; but as the approximate ratio 1 : 8 only differs from this in hundredth parts of 1 per cent. of the amounts of the elements, the composition of water may be approximately expressed by the above easily remembered ratio 1 : 8, or more correctly 1.008 : 8, which is adopted in this work and in most researches of the present day. By whatever method water be obtained, it will always present the same composition. Whether it be taken from nature and purified, or whether it be obtained from hydrogen by oxidation, or whether it be separated from any of its compounds, or obtained by some double decomposition, it will in every case contain 1 part by weight of hydrogen and about 8 parts of oxygen. This is because water is a definite chemical compound. Detonating gas, from which it may be formed, is a simple mixture of oxygen and hydrogen, although a mixture of the same composition as water. All the properties of both constituent gases are preserved in detonating gas. Either one or the other gas may be added to it without destroying its homogeneity. The fundamental properties of oxygen and hydrogen are not found in water, and neither of the gases can be directly combined with it. But they may be evolved from it. In the formation of water there is an evolution of heat; for the decomposition of water heat is required. All this is expressed by saying that *water is a definite chemical compound of hydrogen with oxygen*. Taking the symbol of hydrogen, H, as expressing many times. The average result was that water contains 1253.3 parts of hydrogen per 10,000 parts of oxygen. Making a correction for the amount of air contained in the sulphuric acid employed for producing the hydrogen, Dumas obtained the average figure 1251.5, the extreme values being 1247.2 and 1256.2. This proves that per 1 part of hydrogen, water contains 7.9904 parts of oxygen, with an error of not more than $\frac{1}{250}$, or 0.03, in the amount of oxygen per 1 part of hydrogen.

Erdmann and Marchand, in eight determinations, found that, per 10,000 parts of oxygen, water contains an average of 1,252 parts of hydrogen, the separate values ranging from 1258.5 to 1248.7; hence for 1 part of hydrogen there would be 7.9952 of oxygen, with an error of at most 0.05.

Keiser (1888), in America, by employing palladium hydride, and by introducing various fresh precautions for obtaining accurate results, found the composition of water to be 15.95 parts of oxygen per 2 of hydrogen.

The latest determinations of the composition of water, as also those made by Dumas, always give less than 8, and on the average from 7.93 to 7.95 of oxygen per 1 part of hydrogen, as has been mentioned in the text, and the final mean may be taken as 7.936, with a possible error of not more than 1 in the last decimal figure.

ing a unit quantity (or more exactly 1.008) by weight of this substance, and expressing 16 parts by weight of oxygen by O, we can formulate all the above statements by the chemical symbol of water, H_2O . As only definite chemical compounds are denoted by formulæ, having indicated the formula of a compound substance we express by it the entire series of properties which go to make up our conception of a definite compound, and at the same time the quantitative composition of the substance by weight. Further, as we shall see later, formulæ express the volume of the gases contained in a substance. Thus the formula of water shows that it contains two volumes of hydrogen and one volume of oxygen. Besides which, we shall find that the formula expresses the density of the vapour of a compound, and on this many properties of substances depend, and, as we shall learn, determine the quantities of the bodies entering into reactions. This vapour density we shall see determines also the quantity of a substance entering into a reaction. Thus the letters H_2O tell the chemist the entire history of the substance. This is an international language, which endows chemistry with a simplicity, clearness, stability, and trustworthiness founded on the investigation of the laws of nature.

CHAPTER III

OXYGEN AND THE CHIEF ASPECTS OF ITS SALINE COMBINATIONS

ON the earth's surface there is no other element which is so widely distributed as is oxygen in its various compounds.¹ It constitutes eight-ninths of the weight of water, which occupies the greater part of the earth's surface. Nearly all earthy substances and rocks consist of compounds of oxygen with metals and other elements. Thus, the greater part of sand is formed of silica, SiO_2 , which contains 53 per cent. of oxygen ; while clay and the earthy substances and rocks contain about 40 per cent. by weight of oxygen ; animal and vegetable substances are also very rich in oxygen. Without counting the water present in them, plants contain up to 40, and animals up to 20, per cent. by weight of oxygen. Thus, oxygen compounds predominate on the earth's surface. Besides this, a portion exists in a free state, and is contained in admixture with nitrogen in the atmosphere, forming about one-fourth of its mass, or one-fifth of its volume.

Being so widely distributed in nature, oxygen plays a very important part in it, for a number of the phenomena which take place around us are mainly dependent on it. **Animals breathe** air in order to obtain from it only the **oxygen**, which enters their respiratory organs (the lungs of human beings and animals, the gills of fishes, and the tracheæ of insects) ; they, so to say, drink in air in order to absorb the oxygen. The oxygen contained in the air (or dissolved in water) passes through the membranes of the respiratory organs into the blood, is retained in it by the blood corpuscles, is transmitted by their means to all parts of the body, aids their transformations, bringing about chemical processes in them, and extracting from them chiefly carbon, in the form of carbonic anhydride, the greater part of which passes into the blood, is dissolved by it, and is thrown off by the lungs during the absorption of the oxygen. Thus, in the process of respiration,

¹ As regards the interior of the earth, it probably contains far less oxygen compounds than the surface, judging by the accumulated evidences of the earth's origin, of meteorites, of the earth's density, &c. (see Chapter VIII., note 58, and Chapter XXII., note 2).

carbonic anhydride (and water) is given off and the oxygen of the air absorbed, by which means the blood is changed from the red venous to the dark-red arterial form. The cessation of this process causes death, because then all these chemical processes, and the consequent heat and work which the oxygen introduced into the system gives rise to, cease. For this reason suffocation and death ensue in a vacuum, or in a gas which does not contain free oxygen, i.e., which does not support combustion. If an animal is placed in an atmosphere of free oxygen, at first its movements are very active and a general invigoration is remarked, but a reaction soon sets in, and death may ensue. The oxygen of the air when it enters the lungs is diluted with four volumes of nitrogen, which is not absorbed into the system, so that the blood absorbs but a small quantity of oxygen from the air, whilst in an atmosphere of pure oxygen a large quantity of oxygen would be absorbed, and would produce a very rapid change of all parts of the organism, and destroy it. From what has been said, it will be understood that pure oxygen gas may be employed in respiration, at any rate for a limited time. When the respiratory organs suffer under certain forms of suffocation and impediment to breathing, pure oxygen is frequently had recourse to.²

The combustion of organic substances—that is, substances which make up the composition of plants and animals—proceeds in the same manner as the combustion of many inorganic substances, such as sulphur, phosphorus, iron, &c., from the combination of these substances with oxygen, as was described in the Introduction. The decomposition, rotting, and similar transformations of substances, which proceed around us, are also very often dependent on the action of the oxygen of the air, and reduce this gas from a free to a combined state. The majority of the compounds of oxygen are, like water, very stable, and

² It is evident that the partial pressure (see Chapter I.) acts in respiration. The researches of Paul Bert showed this with particular clearness. Under a pressure of one-fifth of an atmosphere, consisting of oxygen only, animals and human beings remain under the ordinary conditions of the partial pressure of oxygen, but organisms cannot support air rarefied to one-fifth, for then the partial pressure of the oxygen falls to one-twenty-fifth of an atmosphere. Even under a pressure of one-third of an atmosphere the regular life of human beings is impossible, because of the impossibility of respiration (owing to the decrease of solubility of oxygen in the blood), on account of the small partial pressure of the oxygen, and not from any mechanical effect of the decrease of pressure. Paul Bert illustrated all this by many experiments, some of which he conducted on himself. This explains, among other things, the discomfort felt in the ascent of high mountains or in balloons, when the height reached exceeds eight kilometres, and at pressures below 250 mm. It is evident that an artificial atmosphere has to be employed in the ascent to great heights, just as in submarine work. The cure by compressed and rarefied air which is practised in certain illnesses is based partly on the mechanical action of the change of pressure and partly on the alteration in the partial pressure of the respired oxygen.

do not give up their oxygen under the ordinary conditions of nature. As the above-mentioned influences are at work everywhere, it might be expected that the amount of free oxygen in the atmosphere should decrease, and that this decrease should proceed somewhat rapidly. This is, in fact, observed where combustion or respiration proceeds in a closed space. Animals suffocate in a closed space because in consuming the oxygen the air remains unfit for respiration. In the same manner combustion, after a time, ceases in a closed space, as may be proved by a very simple experiment. An ignited substance—for instance, a piece of burning sulphur—has only to be placed in a glass flask, which is then closed with a stout cork to prevent the access of the external air; combustion will proceed for a certain time, so long as the flask contains any free oxygen, but it will cease when the oxygen of the enclosed air has entirely combined with the sulphur. From what has been said, it is evident that regularity of combustion or respiration requires a constant renewal of air—that is, that the burning substance or respiring animal should have access to a fresh supply of oxygen. This is attained in dwellings by having many windows, outlets, and ventilators, and by the current of air produced by fires and stoves. As regards the air over the entire earth's surface its proportion of oxygen hardly decreases at all, because in nature there is a process going on which renews the supply of free oxygen. **Plants**, or rather their leaves, during the daytime,³ under the influence of light, absorb carbonic anhydride, CO_2 , and **evolve free oxygen**. Thus the loss of oxygen which occurs in consequence of the respiration of animals and of combustion is made good by plants. If a leaf be placed in a bell jar containing water, and carbonic anhydride (because this gas is absorbed and oxygen evolved from it by plants) be passed into the bell, and the whole apparatus placed in sunlight, then oxygen will accumulate in the bell jar. This experiment was first made by Priestley at the end of the last century. Thus the life of plants on the earth not only serves for the formation of food for animals, but also for keeping up a constant percentage of oxygen in the atmosphere. In the long period of the life of the earth an equilibrium has been attained between the processes absorbing and evolving oxygen, by which a definite quantity of free oxygen is preserved in the entire mass of the atmosphere.⁴

³ At night, without the action of light, without the absorption of that energy which is required for the decomposition of carbonic anhydride into free oxygen and carbon (which is retained by the plants), they breathe like animals, absorbing oxygen and evolving carbonic anhydride. This process also goes on side by side with the reverse process in the daytime, but it is then far feebler than that which gives oxygen.

⁴ The earth's surface has an area of about 510 million square kilometres, and the mass of the air (at a pressure of 760 mm.) on each kilometre of surface is about $10\frac{1}{3}$ thousand

Oxygen was obtained as an independent gas in 1774 by Priestley in England and in the same year by Scheele in Sweden, but its nature and great importance were only perfectly elucidated by Lavoisier.

Free oxygen may be obtained by one or another method from all the substances in which it occurs. Thus, for instance, the oxygen of many substances may be transferred into water, from which, as we have already seen, oxygen may be obtained.⁵ We will first consider the methods of extracting oxygen from air as being a substance everywhere distributed. The separation of oxygen from it is, however, hampered by many difficulties.

From air, which consists of a *mixture* of oxygen and nitrogen, the nitrogen alone cannot be removed, because it has no inclination to combine directly or readily with any substance; and although it does combine with certain substances (boron, magnesium, titanium), these substances combine simultaneously with the oxygen of the atmosphere.⁶

millions of kilograms, or about $10\frac{1}{2}$ million tons; therefore the whole weight of the atmosphere is about 5,100 million million ($= 51 \times 10^{14}$) tons. Consequently there are about 2×10^{15} tons of free oxygen in the earth's atmosphere. The innumerable series of processes which absorb a portion of this oxygen are compensated for by the plant processes. Assuming that 100 million tons of vegetable matter, containing 40 per cent. of carbon, formed from carbonic acid, are produced (and the same process proceeds in water) per year on the 100 million square kilometres of dry land (ten tons of roots, leaves, stems, &c., per hectare, or $\frac{1}{100}$ of a square kilometre), we find that the plant life of the dry land gives about 100,000 tons of oxygen, which is an insignificant fraction of the entire mass of the oxygen of the air.

⁵ The extraction of oxygen from water may be effected by two processes: either by the decomposition of water into its constituent parts by the action of a galvanic current (Chapter II.), or by means of the removal of the hydrogen from water. But, as we have seen and already know, hydrogen enters into direct combination with very few substances, and then only under special circumstances; whilst oxygen, as we shall soon learn, combines with a great many substances. Only gaseous chlorine (and, more especially, fluorine) is capable of decomposing water, taking up the hydrogen from it, without combining with the oxygen. Chlorine is soluble in water, and if an aqueous solution of chlorine, so-called chlorine water, be poured into a flask, and this be inverted in a basin containing the same chlorine water, we shall then have an apparatus by means of which oxygen may be extracted from water. At the ordinary temperature, and in the dark, chlorine does not act on water, or only acts very feebly; but under the action of direct sunlight chlorine decomposes water, with the evolution of oxygen. The chlorine then combines with the hydrogen, and gives hydrochloric acid, which dissolves in the water, and therefore free oxygen will be separated from the liquid, together with a small quantity of chlorine in admixture, which can be easily removed by passing the gas through a solution of caustic potash.

⁶ Differences in the physical properties of the two gases cannot be here taken advantage of, because they are very similar in these properties. Thus the density of oxygen is 16 times and that of nitrogen 14 times greater than the density of hydrogen, so that porous vessels cannot be employed, the difference between the times of their passage through a porous surface being too insignificant.

Graham, however, succeeded in enriching air in oxygen by passing it through india-rubber. This may be done in the following way:—A common indiarubber cushion, E (fig. 31), is taken, and its orifice hermetically connected with an air-pump, or, better

However, oxygen may be separated from air by causing it to combine with substances which may be easily decomposed by the action of heat,

still, a mercury aspirator (the Sprengel pump, designated by the letters A, C, B). When the aspirator (Chapter II., note 16) has pumped out the air, which will be seen by the mercury running out in an almost uninterrupted stream and by its standing approximately at the barometric height, then it may be clearly observed that gas passes through the

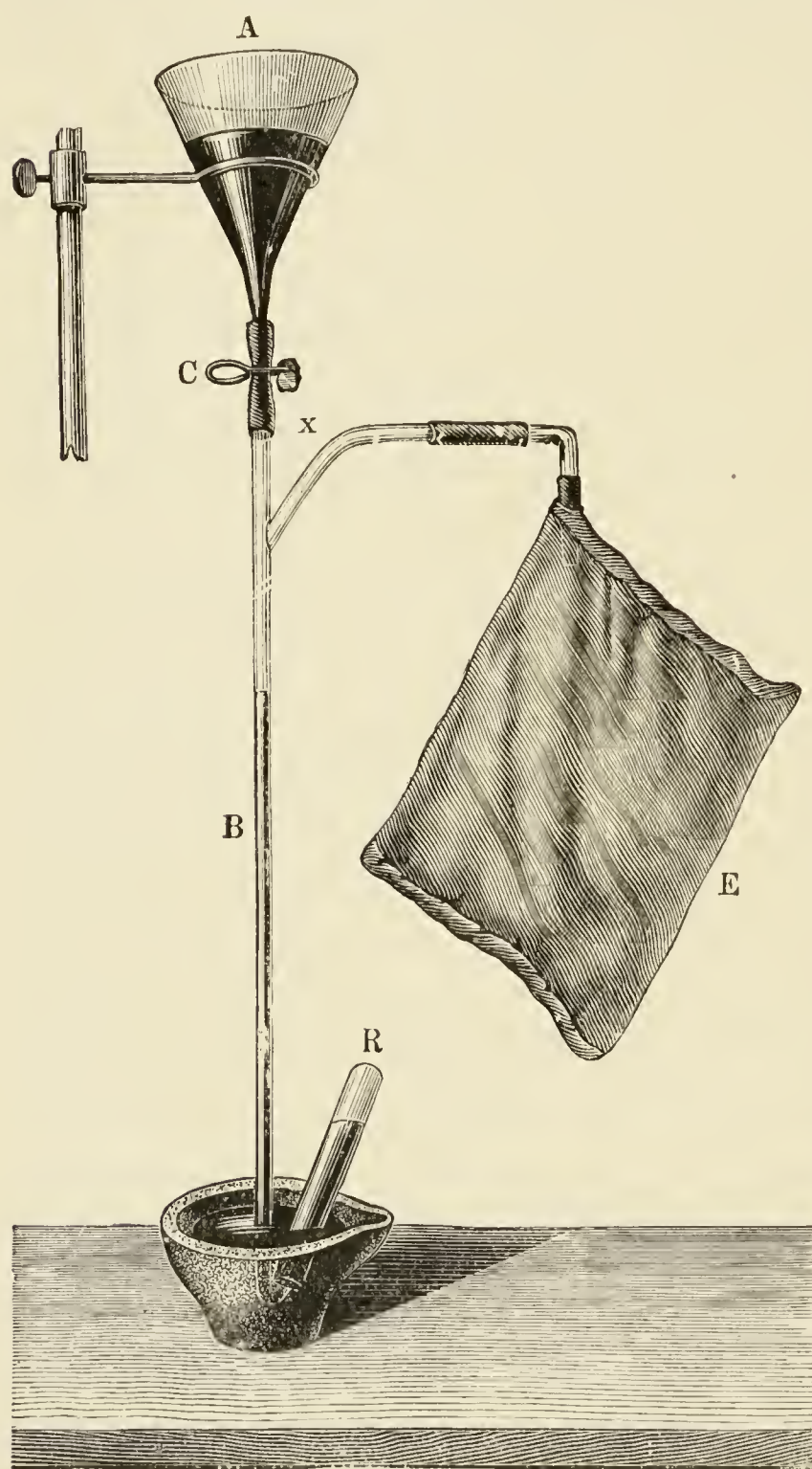


FIG. 31.—Graham's apparatus for the decomposition of air by pumping it through indiarubber.

indiarubber. This is also seen from the fact that bubbles of gas continually pass along with the mercury. A minus pressure may be constantly maintained in the cushion by pouring mercury into the funnel A, and screwing up the pinchcock C, so that the stream flowing from it is small, and then a portion of the air passing through the indiarubber will be carried down with the mercury. This air may be collected in the cylinder R. Its composition is found to be about 42 volumes of oxygen, 57 volumes of nitrogen, and 1 volume of carbonic anhydride, whilst ordinary air contains only 21 volumes of oxygen in 100 volumes. A square metre of indiarubber surface (of the ordinary thickness) passes about 45 c.c. of such air per hour. Such an experiment clearly shows that indiarubber is permeable to gases. This may, by the way, be observed in common toy balloons filled with coal-gas. They fall after a day or two, not because there are holes in them, but because air penetrates into, and the gas from, their interior, through the surface of the indiarubber of which they are made. As was shown by Mitchell and Graham, the rate of the passage of gases through indiarubber does not depend on their densities, and consequently its permeability

is not determined by orifices. It more resembles dialysis (Chap. I., note 18) and occlusion (Chap. II., note 37). Equal volumes of gases penetrate through indiarubber in periods of time related to each other as follows:—carbonic anhydride, 100; hydrogen, 247; oxygen, 532; marsh gas, 633; carbonic oxide, 1,220; nitrogen, 1,358. Hence nitrogen penetrates more slowly than oxygen, and carbonic anhydride more quickly than other gases. 2·556 volumes of oxygen and 13·585 volumes of carbonic anhydride pass through in the same time as one volume of nitrogen. By multiplying these ratios by the amounts of these gases in air, we obtain figures which are in almost the same

and in so doing give up the oxygen absorbed—that is, by making use of reversible reactions. Thus, for instance, the oxygen of the atmosphere may be made to oxidise sulphurous anhydride, SO_2 (by passing directly over ignited spongy platinum), and so form sulphuric anhydride, or sulphur trioxide, SO_3 ; and this substance (which is a solid and volatile, and therefore easily separated from the nitrogen and sulphurous anhydride), on further heating, gives oxygen and sulphurous anhydride. Caustic soda or lime extracts (absorbs) the sulphurous anhydride from this mixture, whilst the oxygen is not absorbed, and is hence isolated from the air. On a large scale in works, as we shall afterwards see, sulphurous anhydride is transformed into hydrate of sulphur trioxide, or sulphuric acid, H_2SO_4 ; if this is allowed to drop on to red-hot flagstones, water, sulphurous anhydride, and oxygen may be obtained. The oxygen is easily isolated from this mixture by passing the gases over lime. The extraction of oxygen from oxide of mercury (Priestley, Lavoisier), which is obtained from mercury and the oxygen of the atmosphere, is also a reversible reaction by which oxygen may be obtained from the atmosphere (see Introduction). So also, by passing dry air through a red-hot tube containing barium oxide, it is made to combine with the oxygen of the air. In this reaction the so-called barium peroxide, or dioxide, BaO_2 , is formed from barium oxide, BaO , and at a higher temperature the former evolves the absorbed oxygen, and leaves the barium oxide originally taken.⁷

proportion as the volumes of the gases penetrating from air through indiarubber. If the process of dialysis be repeated on the air which has already passed through indiarubber, then a mixture containing 65 per cent. by volume of oxygen is obtained. It may be thought that the cause of this phenomenon is the absorption or occlusion (see Chap. II., note 37) of gases by indiarubber and the evolution of the gas dissolved in a vacuum; and, indeed, indiarubber does absorb gases, especially carbonic anhydride. Graham called the above method of the decomposition of air *atmolysis*.

Now that *liquid air* can be produced in large quantities (Chap. V.), the difference between the boiling-points of nitrogen (about -194°) and oxygen (about -181°), i.e., the greater elasticity (vapour pressure) of the nitrogen, can be taken advantage of for isolating the oxygen of the air. If liquid air be kept in a double-walled vessel (Chap. II., note 32), the nitrogen will evaporate to a greater extent than the oxygen, and a liquid far richer in oxygen than nitrogen will be obtained in the residue. If the mixture be carefully distilled (or only partially liquefied) it may be reduced to a residue containing 80 per cent. of oxygen. And as the evaporation of such liquids produces the low temperatures needed for liquefying air, this method may serve as a cheap means for obtaining from the air a gas rich in oxygen, combustion in which would give a very high temperature which might be advantageously employed for many purposes (for lighting or metallurgy). The day may come when this mode of enriching the air in oxygen may be employed on a large scale in works, &c., and so crown the many efforts which have been made in this direction.

⁷ The preparation of oxygen by this method, which is due to **Boussingault**, is conducted in a porcelain tube, placed in a stove heated by charcoal. Barium oxide (which may be obtained by igniting barium nitrate, previously dried) is placed in the tube, through which a current of air passes. The air is previously passed through a solution of caustic potash, to remove all traces of carbonic anhydride, and is very carefully dried (for the

Oxygen is evolved with particular ease by a whole series of unstable oxygen compounds, of which we shall proceed to take a general survey, remarking that certain of these reactions, although not all, belong to the class of reversible reactions;⁸ so that in order to obtain many of these substances (for instance, potassium chlorate) rich in oxygen,

hydrate, BaH_2O_2 , does not give the peroxide). At a *dark-red heat* ($500\text{--}600^\circ$), the oxide of barium absorbs oxygen from the air, so that the gas leaving the tube consists chiefly of nitrogen. When the absorption ceases, the air will pass through the tube unchanged, which may be recognised from the fact that it supports combustion. Under these circumstances, the barium oxide is converted into peroxide and eleven parts of the oxide absorb about one part of oxygen by weight. When the absorption ceases, one end of the tube is closed, a cork with a gas-conducting tube is fixed into the other end, and the heat of the stove is increased to a *bright-red heat* (800°). At this temperature the peroxide gives up all that oxygen which it acquired at a dark-red heat,—i.e., about one part of oxygen is evolved from twelve parts of barium peroxide. After the evolution of the oxygen there remains the barium oxide which was originally taken, so that air may be again passed over it, and thus the preparation of oxygen from one and the same quantity of barium oxide may be repeated many times. Oxygen has been produced one hundred times from one mass of oxide by this method, all the necessary precautions being taken as regards the temperature of the mass and the removal of moisture and carbonic acid from the air. Unless such precautions be taken, the mass of oxide soon becomes spoilt.

As oxygen may become of considerable technical use, from its capacity for giving high temperatures and intense light in the combustion of substances, its preparation directly from air by practical methods forms a problem, whose solution many investigators are continuing to work at up to the present day (note 6). The most practical methods are those of **Tessié du Motay** and **Kassner**. The first is based on the fact that a mixture of equal weights of manganese peroxide and caustic soda at an incipient red heat (about 350°) absorbs oxygen from air, with the separation of water, according to the equation: $\text{MnO}_2 + 2\text{NaHO} + \text{O} = \text{Na}_2\text{MnO}_4 + \text{H}_2\text{O}$. If superheated steam, at a temperature of about 450° , be then passed through the mixture, the manganese peroxide and caustic soda originally taken are regenerated, and the oxygen held by them is evolved, according to the reverse equation: $\text{Na}_2\text{MnO}_4 + \text{H}_2\text{O} = \text{MnO}_2 + 2\text{NaHO} + \text{O}$. This mode of preparing oxygen may be repeated an infinite number of times. The oxygen in combining liberates water, and steam, acting on the resultant substance, evolves oxygen. Hence all that is required for the preparation of oxygen by this method is fuel and the alternate cutting off of the supplies of air and steam. In Kassner's process (1891) a mixture of oxide of lead and lime ($\text{PbO} + 2\text{CaO}$) is heated to redness in the presence of air, oxygen being thus absorbed and calcium plumbate, Ca_2PbO_4 , formed. The latter is of a chocolate colour, and on further heating evolves oxygen and gives the original mixture, $\text{PbO} + 2\text{CaO}$, so that the phenomenon is essentially the same as in Boussingault's process (with BaO), but according to Le Chatelier (1893) the dissociation pressure of the oxygen evolved from Ca_2PbO_4 is less than with BaO_2 at the same temperatures; for instance, at 940° , it is 112 mm. of mercury for the first, and for the latter 210 mm. at 720° , and 670 mm. at 790° , while for Ca_2PbO_4 this last pressure is only reached at $1,080^\circ$. However, in Kassner's process the oxygen is absorbed more rapidly, and the influence of the presence of moisture and carbonic anhydride in the air is not so marked, so that this process, like that of Tessié du Motay, deserves consideration.

⁸ Even the decomposition of manganese peroxide is reversible (under certain changes in the conditions of reaction), and it may be re-obtained from that suboxide (or its salts), which is formed in the evolution of oxygen (Chap. XI., note 6). The compounds of chromic acid containing the trioxide, CrO_3 , in evolving oxygen, give chromium oxide, Cr_2O_3 , but they re-form the salt of chromic acid when heated to redness in air with an alkali.

recourse must be had to indirect methods (see Introduction) with which we shall become acquainted in the course of this book.

1. **The compounds of oxygen** with certain metals, namely, mercury, silver, gold, and platinum, having once been obtained, retain their oxygen at the ordinary temperature, but part with it at a red heat. These compounds are solids, generally amorphous and infusible, and are easily decomposed by heat into the metal and oxygen. We have seen an example of this in the decomposition of mercury oxide. Priestley, in 1774, obtained pure oxygen for the first time by heating mercury oxide by means of a burning-glass. He showed its difference from air and its characteristic property of supporting combustion 'with remarkable vigour,' and he named it dephlogisticated air.

2. The substances called **peroxides**⁹ evolve oxygen at a greater or less heat (and also by the action of many acids). They usually contain metals combined with a large quantity of oxygen. Peroxides are the highest oxides of certain metals which generally give several compounds with oxygen. Those of the lowest degrees of oxidation, containing the least amount of oxygen, are generally substances capable of reacting easily with acids, for instance, with sulphuric acid. Such low oxides are called bases. Peroxides contain more oxygen than the bases formed by the same metals. For example, lead oxide contains 7.1 parts of oxygen in 100 parts, and is basic, but lead peroxide contains 13.3 parts of oxygen in 100 parts. **Manganese peroxide or dioxide** is a similar substance, and is a solid of a dark brown colour, which occurs in nature. It is employed for technical purposes under the name of black oxide of manganese (in German 'Braunstein,' the 'pyrolusite' of the mineralogist). Peroxides are able to evolve oxygen at a more or less elevated temperature. They do not then part with all their oxygen, but with only a portion of it, and are converted into a lower oxide or base. Thus for example, lead peroxide, on heating, gives oxygen and lead oxide. The decomposition of this peroxide proceeds tolerably easily on heating, even in a glass vessel, but manganese peroxide only evolves oxygen at a strong red heat, and therefore oxygen can only be obtained from it in iron or clay vessels. This was formerly the method for obtaining oxygen. Manganese peroxide only parts with one-third of its oxygen (according to the equation, $3\text{MnO}_2 = \text{Mn}_3\text{O}_4 + \text{O}_2$), two-thirds remaining

⁹ We shall afterwards see that it is only substances like barium peroxide (which give hydrogen peroxide) which should be counted as true peroxides, and that MnO_2 , PbO_2 , &c., should be distinguished from them (they do not give hydrogen peroxide with acids), and therefore it is best to call these dioxides. This we generally do in the context, only retaining the old nomenclature in a few instances, on account of its historical interest, and to enable our readers to refer to former treatises. Peroxide of hydrogen (Chap. IV.) easily parts with half of its oxygen, leaving water as a residue.

in the solid residue after heating. Metallic peroxides are also capable of evolving oxygen on heating with sulphuric acid. They then evolve just that amount of oxygen which is in excess of that necessary for the formation of the base, which latter reacts on the sulphuric acid forming a compound (salt) with it. Thus barium peroxide, when

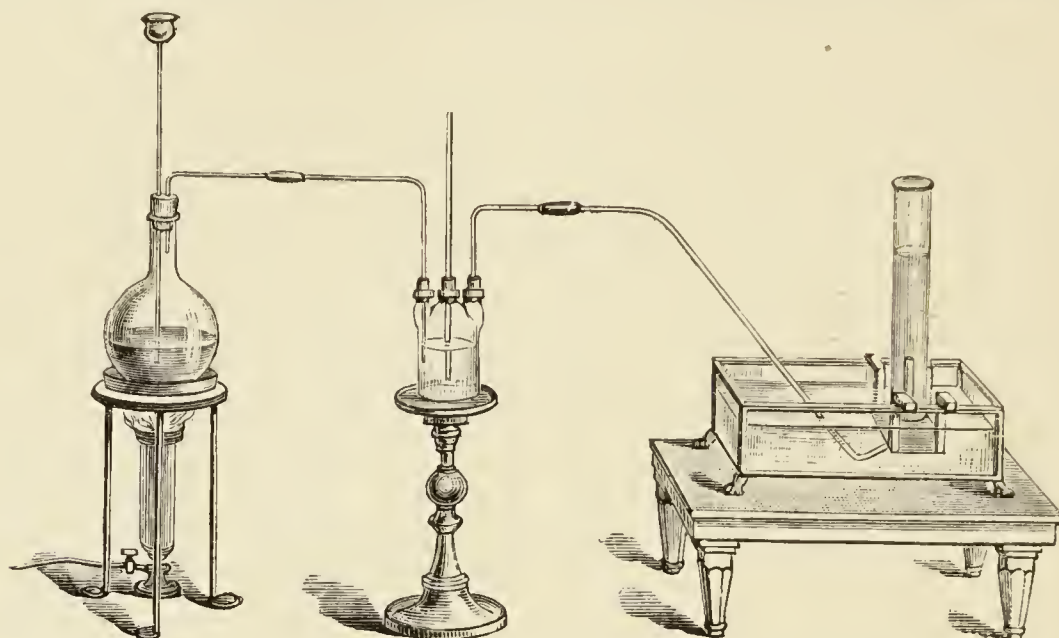


FIG. 32.—Preparation of oxygen from manganese peroxide and sulphuric acid. The gas evolved is passed through a Woulfe's bottle containing caustic potash solution.

heated with sulphuric acid, forms oxygen and barium oxide, which gives a compound with sulphuric acid termed barium sulphate ($\text{BaO}_2 + \text{H}_2\text{SO}_4 = \text{BaSO}_4 + \text{H}_2\text{O} + \text{O}$).^{9a} For the purposes of experiment, powdered manganese peroxide is usually taken and mixed with strong sulphuric acid in a flask, and the apparatus set up as shown in fig. 32.

^{9a} Peroxide of barium also gives oxygen at the ordinary temperature in the presence of the solutions of many substances in a higher degree of oxidation. In this connection we may mention that Kassner (1890) proposes to obtain oxygen for laboratory purposes by mixing BaO_2 with $\text{FeK}_3(\text{CN})_6$ (red prussiate of potash, Chapter XXII.); the reaction proceeds with the evolution of oxygen on the addition of even a very small quantity of water. In order to ensure a gradual evolution of gas, the author proposes to introduce the two substances into the reaction, little by little, instead of all at once; and this may be done with the following arrangement (Gavaloffsky). Finely powdered peroxide of barium is placed in an ordinary flask and sufficient water is added to fill the flask one-third full. The cork closing the flask has three holes: (1) for the gas-conducting tube; (2) for a rod to stir the BaO_2 ; and (3) for a glass rod terminating in a perforated glass vessel containing crystals of $\text{FeK}_3(\text{CN})_6$. When it is desired to start the evolution of the oxygen, the vessel is lowered until it is immersed in the liquid in the flask, and the BaO_2 is stirred with the other rod. The reaction proceeds according to the equation, $\text{BaO}_2 + 2\text{FeK}_3(\text{CN})_6 = \text{FeK}_4(\text{CN})_6 + \text{FeK}_2\text{Ba}(\text{CN})_6 + \text{O}_2$. The double salt, $\text{FeBa}_2(\text{CN})_6$, crystallises out from the mother liquor. To understand the course of the reaction, it must be remembered that BaO_2 is of a higher degree of oxidation, and that it parts with oxygen and gives the base BaO , which enters into the complex salt $\text{FeK}_2\text{Ba}(\text{CN})_6 = \text{Fe}(\text{CN})_2 + 2\text{KCN} + \text{Ba}(\text{CN})_2$, and this latter $= \text{BaO} + 2\text{HCN} - \text{H}_2\text{O}$. Moreover, $\text{FeK}_3(\text{CN})_6$ contains the salt $\text{Fe}_2(\text{CN})_6$, which also corresponds with the higher degree of oxidation of iron, Fe_2O_3 , whilst after the reaction a salt is obtained which contains $\text{Fe}(\text{CN})_2$, and corresponds with the lower degree of oxidation, FeO , so that (in the presence of water) oxygen is set free on this side also, i.e., the reaction gives compounds of lower degrees of oxidation and oxygen.

The gas which is evolved is passed through a Woulfe's (two-necked) bottle containing a solution of caustic potash, to purify it from carbonic anhydride and chlorine, which accompany oxygen from commercial manganese peroxide, and the gas is not collected until a thin smouldering taper placed in front of the escape orifice bursts into flame, and so shows that the gas coming off is oxygen. By this method of decomposition of the manganese peroxide by sulphuric acid there is evolved, not, as on heating, one-third, but one-half of the oxygen contained in the peroxide ($\text{MnO}_2 + \text{H}_2\text{SO}_4 = \text{MnSO}_4 + \text{H}_2\text{O} + \text{O}$); that is, 50 grams of peroxide gives about $7\frac{1}{2}$ grams, or about $5\frac{1}{2}$ litres, of oxygen,¹⁰ whilst by heating only about $3\frac{1}{2}$ litres are obtained. The chemists of Lavoisier's time generally obtained oxygen by heating manganese peroxide. At the present time more convenient methods are known.

3. A third source to which recourse may be had for obtaining oxygen is afforded by **acids** and **salts** containing much oxygen, which are capable, by parting with a portion or all of their oxygen, of being converted into other more difficultly decomposable compounds (lower products of oxidation). These acids and salts (like peroxides) evolve oxygen either on heating alone, or only when in the presence of some other substance. Sulphuric acid may be taken as an example of an acid which is decomposed by the action of heat alone,¹¹ for it breaks up at a red heat into water, sulphurous anhydride, and oxygen, as was mentioned before. Priestley, in 1772, and Scheele, somewhat later, obtained oxygen by heating nitre to a red heat. The best example of the formation of oxygen by the heating of salts is given by **potassium chlorate**, or Berthollet's salt, so called after the French chemist who discovered it. Potassium chlorate is a salt composed of the elements potassium, chlorine, and oxygen: KClO_3 . It occurs as transparent colourless plates, is soluble in water, especially in hot water, and resembles common table salt in some of its reactions and physical properties; it melts on heating, and in melting begins to decompose, evolving oxygen gas. This decomposition ends in all the oxygen being evolved from the potassium chlorate, potassium chloride being left as a

¹⁰ Scheele, in 1785, discovered the method of obtaining oxygen by treating manganese peroxide with sulphuric acid.

¹¹ All acids rich in oxygen, and especially those whose elements form lower oxides, evolve oxygen either directly at the ordinary temperature (for instance, ferric acid), or on heating (nitric, manganic, chromic, chloric, and others), or, if lower basic oxides are formed from them, by heating with sulphuric acid. Thus the salts of chromic acid (for example, potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$) give oxygen with sulphuric acid; first potassium sulphate, K_2SO_4 , is formed, and then the chromic acid set free gives a sulphuric acid salt of the lower oxide, Cr_2O_3 . This is a convenient method for obtaining oxygen in small quantities in the laboratory.

residue, according to the equation, $\text{KClO}_3 = \text{KCl} + \text{O}_3$.¹² This decomposition proceeds at a temperature which allows of its being conducted in a glass vessel. However, in decomposing, the molten potassium chlorate swells up and boils, and gradually solidifies, so the evolution of the oxygen is not regular, and the glass vessel may crack. In order to overcome this inconvenience, the potassium chlorate is crushed and mixed with the powder of a substance which is infusible, incapable of combining with the oxygen evolved, and a good conductor of heat. Usually it is mixed with manganese peroxide.¹³ The decomposition of the potassium chlorate is then considerably facilitated, and proceeds at a lower temperature (because the entire mass is then better heated, both externally and internally) and without swelling up, so that this method is more convenient than the decomposition of the salt alone. This method for the preparation of oxygen is very convenient, and is generally employed when a small quantity of oxygen is required. Further, potassium chlorate is easily obtained pure, and evolves much oxygen: 100 grams of the salt give as much as 39 grams, or 30 litres, of oxygen. This method is so simple and easy¹⁴ that a course of practical chemistry is often commenced by the preparation of oxygen by this method, and of hydrogen by the aid of zinc and sulphuric acid, since by means of these gases many interesting and striking experiments may be performed.¹⁵

Bleaching powder, which contains calcium hypochlorite, CaCl_2O_2 , evolves oxygen when gently heated in presence of a small quantity of

¹² This reaction is not reversible, and is exothermal—that is, it does not absorb heat, but, on the contrary, evolves 9,713 calories per molecular weight of KClO_3 , equal to 122 parts of salt (according to the determination of Thomsen, who burnt hydrogen in a calorimeter either alone or with a definite quantity of potassium chlorate mixed with oxide of iron). It does not proceed at once, but first forms perchlorate, KClO_4 (see Chlorine and Potassium). It is to be remarked that potassium chloride melts at 766° , potassium chlorate at 359° , and potassium perchlorate at 610° . (Concerning the decomposition of KClO_3 , see Chapter II., note 47.)

¹³ The peroxide does not evolve oxygen in this case (the temperature is not high enough). It may be replaced by many oxides—for instance, by oxide of iron. It is necessary to take the precaution that no combustible substances (such as bits of paper, splinters, sulphur, &c.) fall into the mixture, as they might cause an explosion.

¹⁴ The decomposition of a mixture of fused and well-crushed potassium chlorate with powdered manganese peroxide proceeds at so low a temperature (the salt does not melt) that it may be effected in an ordinary glass flask. The apparatus is arranged in the same manner as in the decomposition of mercury oxide (Introduction), or as shown in the last drawing. As the reaction is exothermal, the decomposition of potassium chlorate with the formation of oxygen may probably be accomplished, under certain conditions (for example, under contact action), at very low temperatures. Substances mixed with the potassium chlorate act partially in this manner.

¹⁵ Many other salts evolve oxygen on heating, like potassium chlorate, but they only part with it either at a very high temperature (as, for instance, common nitre) or else are unsuited for use on account of their cost (potassium manganate), or evolve impure oxygen at a high temperature (zinc sulphate at a red heat gives a mixture of sulphurous anhydride and oxygen).

certain oxides, for instance, cobalt oxide, which in this case acts by contact (see Introduction). When heated by itself, a solution of bleaching powder does not evolve oxygen, but it oxidises the cobalt oxide to a higher degree of oxidation; this higher oxide of cobalt in contact with the bleaching powder decomposes into oxygen and lower oxidised products, and the resultant lower oxide of cobalt with bleaching powder again gives the higher oxide, which again gives up its oxygen, and so on.¹⁶ The calcium hypochlorite is here decomposed according to the equation, $\text{CaCl}_2\text{O}_2 = \text{CaCl}_2 + \text{O}_2$. In this manner a small quantity of cobalt oxide¹⁷ is sufficient for the decomposition of an indefinitely large quantity of bleaching powder. Bleaching powder gives oxygen with still greater facility (without the aid of heat) by the action of an aqueous solution of peroxide of hydrogen (Chap. IV.), which then evolves oxygen, $\text{CaCl}_2\text{O}_2 + \text{H}_2\text{O}_2 = \text{CaCl}_2 + \text{H}_2\text{O} + 3\text{O}$. Permanganate of potassium acts in a similar way.

The properties of oxygen.¹⁸—It is a permanent gas—that is, it cannot be liquefied by pressure at the ordinary temperature, and, further, is only liquefied with difficulty (although more easily than hydrogen) at temperatures below -120° , because this is its absolute (critical) boiling-point. As its critical pressure¹⁹ is about 50 atmospheres, it can be easily

¹⁶ Such is at present the only possible method of explaining the phenomenon of contact action. In many cases, such as the present one, it is supported by observations based on facts (see Chap. IV.) To this class of phenomena may also be referred the evolution of oxygen at the ordinary temperature from a mixture of barium peroxide and potassium manganate with water and sulphuric acid (note 9a). The essence of phenomena of this kind is purely a property of contact; the distribution of the atoms is slightly changed along the planes of contact; and if the equilibrium be unstable it is destroyed. This is more especially frequent with those substances which change exothermally—that is, for those reactions which are accompanied by an evolution of heat. The decomposition $\text{CaCl}_2\text{O}_2 = \text{CaCl}_2 + \text{O}_2$ belongs to this class, like the decomposition of potassium chlorate and peroxide of hydrogen.

¹⁷ Generally a solution of bleaching powder is alkaline (containing free lime), and, therefore, a solution of cobalt chloride is added directly to it, the oxide of cobalt required for the reaction being thus formed.

¹⁸ It must be remarked that in all the reactions above mentioned the formation of oxygen may be prevented by the admixture of substances capable of combining with it—for example, charcoal, many carbon (organic) compounds, sulphur, phosphorus, and various lower oxidation products, &c. These substances absorb the oxygen evolved, combining with it, forming a compound containing oxygen.

The oxygen obtained by any of the above-described methods is therefore rarely pure. It generally contains aqueous vapour, carbonic anhydride, and sometimes small traces of chlorine. The oxygen may be freed from these impurities by passing it through a solution of caustic potash, and by drying it. If the potassium chlorate be dry and pure, it gives almost pure oxygen. However, if the oxygen be required for respiration in cases of sickness, it should be washed by passing it through a solution of caustic alkali and through water. The best way to obtain pure oxygen directly is to take potassium perchlorate (KClO_4), which can be well purified and evolves pure oxygen on heating.

¹⁹ With regard to the absolute boiling-point, critical pressure, and the critical state in general, see Chap. II., notes 29 and 34.

liquefied under pressures greater than 50 atmospheres at temperatures below -120° . According to Dewar, the density of oxygen in a critical state is 0.65 (water=1); but, like all liquids near this point,²⁰ it varies considerably in density with a change of pressure and temperature, and at -181° its density is 1.13 under the ordinary pressure. Liquefied oxygen is an exceedingly mobile transparent liquid, with a faint blue tint^{20a} and boiling (at a pressure of 760 mm.) at -181° or -182° . Oxygen solidifies at the temperature obtained by liquid hydrogen (probably at about -250°), forming a transparent blue ice, which, at a pressure of 55 mm., gives a temperature of -258° . Oxygen, like all gases, is transparent, and, like the majority of gases, colourless. It has no smell or taste, which is evident from the fact of its being a component of air. The weight of one litre of oxygen gas at 0° and 760 mm. pressure, at latitude 45° , is 1.4290 gram (Regnault, Morley, Thomsen, and others); it is slightly denser than air, so that its density in respect to air is 1.1051, and in respect to hydrogen, 16.²¹

In its chemical properties oxygen is remarkable from the fact that it very easily—and, in a chemical sense, vigorously—reacts on a number of substances, forming oxygen compounds. However, only a few substances and mixtures of substances (for example, phosphorus, copper with ammonia, decomposing organic matter, aldehyde, pyrogallol with

²⁰ Judging from what has been said in note 34 of the last chapter, and also from the results of direct observation, it is evident that all substances in a critical state have a large coefficient of expansion, and are very compressible.

^{20a} Even a thin layer of liquid oxygen (or liquid air) gives a perfect absorption spectrum (see Chap. XIII., note 32).

²¹ As water consists of 1 volume of oxygen and 2 volumes of hydrogen, and contains about 16 parts by weight of oxygen per 2 parts by weight of hydrogen, it therefore follows directly that oxygen is nearly 16 times denser than hydrogen. Conversely, the composition of water by weight may be deduced from the densities of hydrogen and oxygen and the volumetric composition of water. This method of mutual and reciprocal correction strengthens the practical data of the exact sciences, the conclusions of which require the greatest possible exactitude and variety of corrections.

It must be observed that the specific heat of oxygen at constant pressure is 0.2175; consequently it is to the specific heat of hydrogen (3.409) as 1 is to 15.6. Hence, the specific heats are inversely proportional to the weights of equal volumes, so that equal volumes of the two gases have (nearly) equal specific heats—that is, they require an equal quantity of heat for raising their temperature by 1° . We shall afterwards consider the specific heat of different substances more fully in Chap. XIV. According to Dewar, the specific heat of liquid hydrogen (between -198° and -182°) is 0.32.

Oxygen, like the majority of difficultly liquefiable gases, is but slightly soluble in water and other liquids. The solubility is given in note 30, Chap. I. From this it is evident that water standing in air must absorb—i.e., dissolve—oxygen. This oxygen serves for the respiration of fishes. Fishes cannot exist in boiled water, because it does not contain the oxygen necessary for their respiration (see Chap. I.) I may also remark that repeated observations (Bore 1886, Baly and Ramsay 1894) on the *positive* discrepancies of oxygen from Boyle's law at low pressures show a rapid change in the law at pressures of about 0.7 mm., although the discrepancies remain positive even before and after this critical pressure.

an alkali, &c.) combine directly and rapidly with oxygen at the ordinary temperature, whilst many substances easily combine with oxygen at a red heat, and this combination often presents a rapid chemical reaction accompanied by the evolution of a large quantity of heat. Every reaction which takes place rapidly, if accompanied by so great an evolution of heat as to produce incandescence, is termed **combustion**. Thus combustion ensues when many metals are plunged into chlorine, or oxide of sodium or barium into carbonic anhydride, or when a spark falls on gunpowder. A great many substances are combustible in oxygen, and, owing to its presence, in air also. In order to start combustion it is generally necessary²² that the combustible substance should be brought to a state of incandescence. The continuation of the process does not require the aid of fresh external heat, because sufficient heat²³ is evolved to raise the temperature of further portions of the combustible substance to the required degree. Examples of this are familiar to all from every-day experience. Combustion proceeds in oxygen with greater rapidity, and is accompanied by a more powerful incandescence, than in ordinary air. This may be demonstrated by a number of very convincing experiments. If a piece of charcoal, attached to a wire and previously brought to red-heat, be plunged into a flask full of oxygen, it burns rapidly at a white heat—i.e., it combines with the oxygen, forming a gaseous product of combustion called carbonic anhydride, carbonic acid gas, or carbon dioxide, CO_2 . This is the same gas as is evolved in the act of respiration, for charcoal is one of the substances which are obtained by the decomposition of all organic substances which contain them, and in the process of respiration part of the constituents of the body, so to speak, slowly burn. If a piece of burning sulphur be placed in a small cup attached to a wire and introduced into a flask full of oxygen, then the sulphur, which burns in air with a very feeble flame, will burn in the oxygen with a violet flame, which,

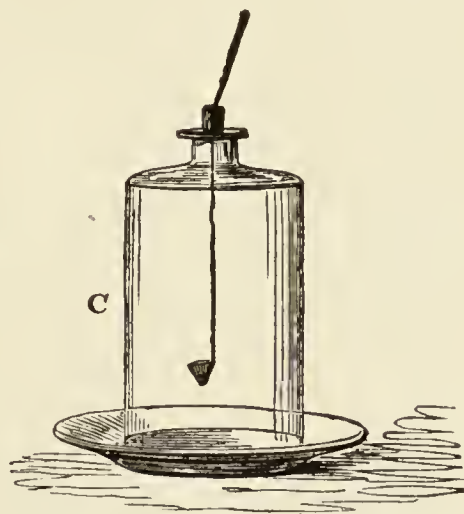


FIG. 33.—Mode of burning sulphur, phosphorus, sodium, &c., in oxygen.

²² Certain substances (with which we shall afterwards become acquainted), however, ignite spontaneously in air; for example, impure phosphoretted hydrogen, silicon hydride, zinc ethyl, and pyrophorus (very finely divided iron, &c.) This signifies that the temperature of ignition is below the ordinary temperature.

²³ If so little heat is evolved that the adjacent parts are not heated to the temperature of combustion, then combustion will cease. Thus combustion may be stayed not only by stopping the access of oxygen, but also by cooling the burning body, i.e., by lowering its temperature. This is what occurs when a candle is blown out, or a fire extinguished by water.

although pale, is much larger than in air. If the sulphur be exchanged for a piece of **phosphorus**,²⁴ then, unless the phosphorus be heated, it will combine very slowly with the oxygen; but, if heated, even if in one spot only, it burns with an exceedingly brilliant white flame. In order to heat the phosphorus inside the flask, the simplest way is to bring a red-hot wire into contact with it. As regards charcoal, this cannot burn until it is brought to a state of incandescence. Sulphur

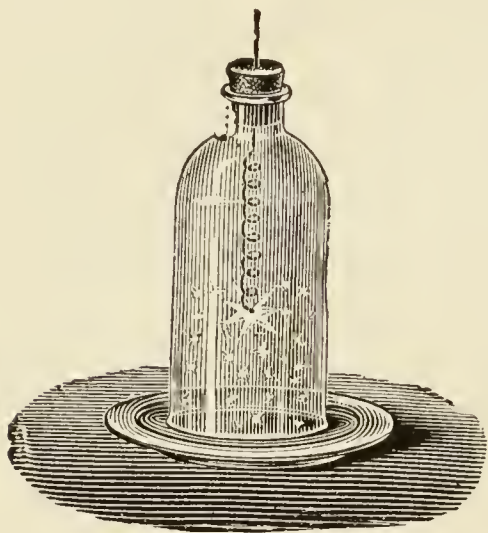


FIG. 34.—Mode of burning a steel spring in oxygen.

also will not burn under 100° , whilst phosphorus inflames at 40° . Phosphorus which has been already lighted in air cannot so well be introduced into the flask, because it burns very rapidly and with a large flame in air. If a small lump of metallic **sodium** be put into a small cup made of lime,²⁵ melted, and ignited,²⁶ it burns very feebly in air. But if burning sodium be introduced into oxygen, the combustion is invigorated and is accompanied by a brighter yellow flame. Metallic **magnesium**, which burns yet more brightly in air, continues to burn with still

greater vigour in oxygen (i.e., the temperature rises still higher), forming a white powder, which is a compound of magnesium with oxygen (magnesium oxide or magnesia). A strip of **iron** or steel does not burn in air, but an iron wire or steel spring may be easily burnt in oxygen.²⁷ The combustion of steel or iron in oxygen is not accompanied by a flame, but sparks of oxide fly in all directions from the burning portions of the iron.²⁸

²⁴ The phosphorus must be dry; it is usually kept in water, as it oxidises in air. It should be cut under water, as otherwise the freshly cut surface oxidises. It must be dried carefully and quickly by wrapping it in blotting-paper. If damp, it splutters on burning. A small piece should be taken, as otherwise the iron spoon will melt. In this and the other experiments on combustion, water should be poured over the bottom of the vessel containing the oxygen, to prevent it from cracking. The cork closing the vessel should not fit tightly, in order to allow for the expansion of the gas due to the heat of the combustion.

²⁵ An iron cup will melt with sodium in oxygen.

²⁶ In order to rapidly heat the lime crucible containing the sodium, it is heated in the flame of a blowpipe described in Chap. VIII.

²⁷ In order to burn a watch-spring, it is first tempered (made red-hot and then slowly cooled) in order to soften it, and then a piece of tinder (or paper soaked in a solution of nitre, and dried) is attached to one end. The tinder is lighted, and the spring then plunged into the oxygen. The burning tinder heats the end of the spring, the heated part burns, and in so doing heats the further portions of the spring, which then burns completely if sufficient oxygen be present.

²⁸ The sparks of rust are produced, owing to the fact that the volume of the oxide of iron is nearly twice that of the iron, and as the heat evolved is not sufficient to entirely

In order to demonstrate by experiment the **combustion of hydrogen** in oxygen, a gas-conducting tube, bent so as to form a convenient jet, is led from the vessel evolving hydrogen. The hydrogen is first ignited in air, and then the gas-conducting tube is let down into a flask containing oxygen. The combustion in oxygen will be similar to that in air; the flame remains pale, notwithstanding the fact that its temperature rises considerably. It is instructive to remark that oxygen may burn in hydrogen, just as hydrogen does in oxygen. In order to show the combustion of oxygen in hydrogen, a tube bent vertically upwards and ending in a fine orifice is attached to the stopcock of a gas-holder full of oxygen. Two wires placed at such a distance from each other as to allow of the passage of a series of sparks from a Ruhmkorff's coil, are fixed in front of the orifice of the tube. This is in order to ignite the oxygen, which may be also done by attaching tinder round the orifice, and burning it. When the wires are arranged at the orifice of the tube, and a series of sparks passes between them, an inverted (because of the lightness of the hydrogen) jar full of hydrogen is placed over the gas-conducting tube. When the jar covers the orifice of the gas-conducting tube (and not before, as otherwise an explosion might take place) the cock of the gasometer is opened, and the oxygen flows into the hydrogen and is set light to by the sparks. The flame obtained is similar to that formed by the combustion of hydrogen in oxygen.²⁹ From this it is evident that the flame is the locality where

melt the oxide or the iron, the particles must be torn off and fly about. Similar sparks are also formed in the combustion of iron in other cases. We called attention in the Introduction to the combustion of iron filings. In the welding of iron, small iron splinters fly off in all directions and burn in the air, as is seen from the fact that whilst flying through the air they remain red-hot, and also because, on cooling, they are seen to be no longer iron, but a compound of it with oxygen. The same thing takes place when the hammer of a gun strikes against the flint. Small scales of steel are heated by the friction, and glow and burn in the air. The combustion of iron is still better seen by taking it as a very fine powder, such as is obtained by the decomposition of certain of its compounds, for instance, by heating Prussian blue, or by the reduction of its compounds with oxygen by hydrogen; when this fine powder is strewn in air, it burns by itself, even without being previously heated (it forms pyrophorus). This depends on the physical state of the surface of the powder after reduction and on the fact that the powder of iron presents a larger surface of contact with air than an equal weight in a compact form.

²⁹ The experiment may be conducted without the wires, if the hydrogen be lighted in the orifice of an inverted cylinder, and at the same time the cylinder be brought over the end of a gas-conducting tube connected with a gas-holder containing oxygen. Thomsen's method may be adopted for a lecture experiment. In this, two glass tubes with platinum ends are passed through orifices, about 1-1½ centimetre apart, in a cork. One tube is connected with a gas-holder containing oxygen and the other with a gas-holder full of hydrogen. Having turned on the gases, the hydrogen is lighted, and a common lamp glass, tapering towards the top, is placed over the cork. The hydrogen continues to burn inside the lamp glass, at the expense of the oxygen. If the current of oxygen is then decreased little by little, a point is reached when, owing to the insufficient supply of

the oxygen combines with the hydrogen, so that a flame of burning oxygen can be obtained as well as a flame of burning hydrogen.

If, instead of hydrogen, any other combustible gas be taken—for example, ordinary coal gas—then the phenomenon of combustion will

be exactly the same, only a bright flame will be obtained, and the products of combustion will be different. However, as coal gas contains a considerable amount of free and combined hydrogen, it will also form a considerable quantity of water in its combustion.

If hydrogen be mixed with oxygen in the proportion in which these gases form water—i.e., if two volumes of hydrogen be taken for each volume of oxygen—the mixture will then be the same as that obtained by the decomposition of water by a galvanic current, i.e., detonating gas.

We have already mentioned in the last chapter that the combination of these gases, or their explosion, may be brought about by the action of an electric spark, because the spark heats the space through which it passes,

and consequently acts in a manner similar to ignition by means of contact with an incandescent or burning substance.³⁰ Cavendish made this experiment on the ignition of detonating gas at the end of the eighteenth

oxygen, the flame of the hydrogen increases in size, disappears for several moments, and then reappears at the tube supplying the oxygen. If the flow of oxygen be now increased again the flame reappears at the hydrogen tube. Air may be taken instead of oxygen, and ordinary coal-gas instead of hydrogen, and it will then be shown how air burns in an atmosphere of coal-gas, and it can easily be proved that the lamp glass is full of a gas combustible in air, because it may be lighted at the top.

³⁰ In fact, instead of a spark, a fine wire may be taken, and an electric current passed through it to bring it to a state of incandescence; in this case there will be no sparks, but the gases will inflame if the wire be fine enough to become red-hot by the passage of the current.

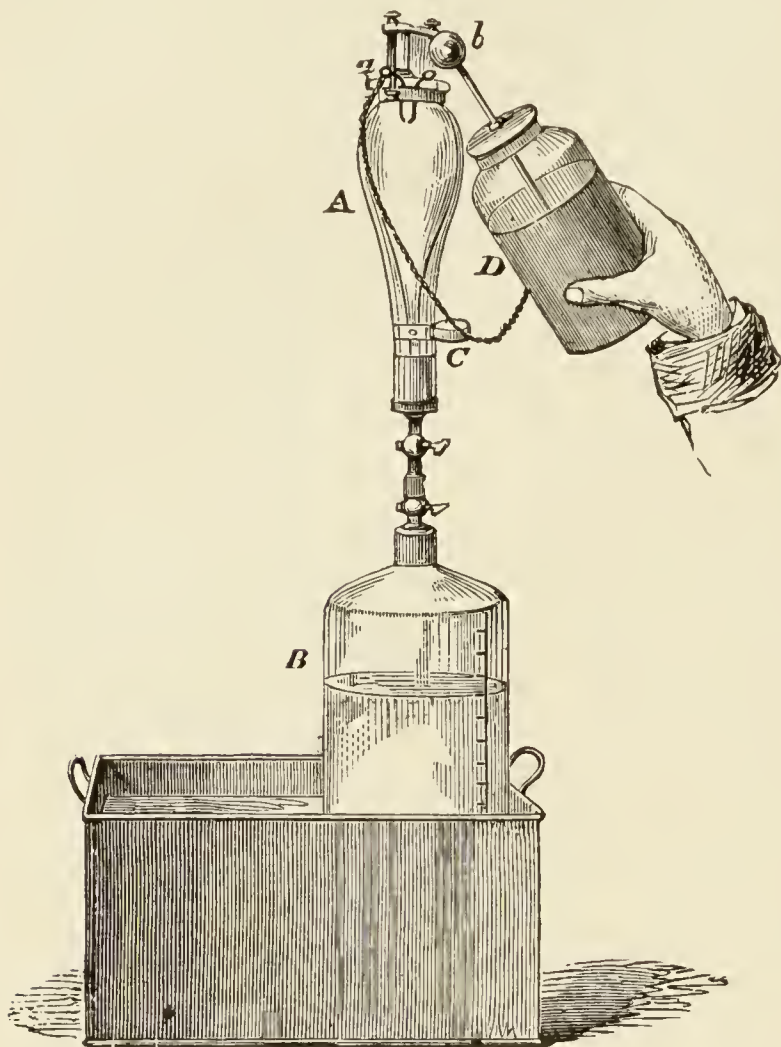


FIG. 35.—Cavendish's apparatus for exploding detonating gas. The bell jar standing in the bath is filled with a mixture of two volumes of hydrogen and one volume of oxygen, and the thick glass vessel A is then serewed on to it. The air is first pumped out of this vessel, so that when the stopcock C is opened, it becomes filled with detonating gas. The stopcock is then re-closed, and the explosion produced by means of a spark from a Leyden jar. After the explosion has taken place the stopcock is again opened, and the water rises into the vessel A.

century, in the apparatus shown in fig. 35. Ignition of gases by the aid of the electric spark is convenient, for the reason that it may then be brought about in a closed vessel, and hence chemists employ this method when it is required to ignite a mixture of oxygen with a combustible gas in a closed vessel. For this purpose, especially since Bunsen's time,³¹ a **eudiometer** is employed. It consists of a thick glass tube graduated along its length in millimetres (for indicating the height of the mercury column), and calibrated for a definite volume (weight of mercury). Two platinum wires are fused into the upper closed end of the tube, as shown in fig. 36.³² By the aid of the eudiometer we may not only determine the volumetric composition of water,³³ and the quantitative content of oxygen in air, but may also make a number of experiments explaining the phenomenon of combustion.

Thus, for example, it may be demonstrated, by the aid of the eudiometer, that, **for the ignition** of detonating gas (like all combustible bodies), a **definite temperature** is required. If the temperature be below that required, combination will not take place, but if at any spot within the tube it rises to the temperature of inflammation, then combination will ensue at that spot, and evolve enough heat for the ignition of the adjacent portions of the detonating mixture. If to 1 volume of detonating gas there be added 10 volumes of oxygen, or 4 volumes of hydrogen, or 3 volumes of carbonic anhydride, we shall not then obtain an explosion by passing a spark through the diluted mixture. This depends on the fact that the temperature falls with dilution of the detonating gas by another gas, because the heat evolved by the combination of the small quantity of hydrogen and oxygen brought to incandescence by the spark is transmitted, not only to the water proceeding from the combination, but also to the foreign substance mixed



FIG. 36.
Eudiometer

³¹ At the present time, a great many other different forms of apparatus, sometimes designed for special purposes, are employed in the laboratory for the investigation of gases. Detailed descriptions of the methods of gas analysis and of the apparatus employed must be looked for in works on analytical and applied chemistry.

³² They must be sealed into the tube in such a manner as to leave no aperture between them and the glass. In order to test this, the eudiometer is almost filled with mercury, and its open end placed in mercury. If there be the smallest orifice at the wires, the external air will enter the cylinder and the mercury will fall, although not rapidly if the orifice be very fine.

³³ Concerning this application of the eudiometer, see the chapter on Nitrogen. It may be mentioned, as illustrating the various uses of the eudiometer, that Professor Timera-seff employed microscopically small eudiometers to analyse the bubbles of gas given off from the leaves of plants.

with the detonating gas.³⁴ The necessity of a definite temperature for the ignition of detonating gas is also seen from the fact that pure detonating gas explodes in the presence of a red-hot iron wire, or of charcoal heated to 275° ; but with a lower degree of incandescence there is no explosion. It may also be brought about by rapid compression, when, as is known, heat is evolved.³⁵ Experiments made in the

³⁴ Further, $\frac{1}{2}$ volume of carbonic oxide, an equal volume of marsh gas, two volumes of hydrogen chloride or of ammonia, or six volumes of nitrogen or twelve of air added to one volume of detonating gas prevent its explosion.

³⁵ If the compression be brought about slowly, so that the heat evolved succeeds in passing to the surrounding space, then the combination of the oxygen and hydrogen does not take place, even when the mixture is compressed 150 times, for the gases are not heated. If paper soaked with a solution of platinum (in aqua regia) and sal-ammoniac is burnt, the ash obtained contains very finely divided platinum, and in this form it is best fitted for igniting hydrogen and detonating gas. Platinum wire requires to be heated, but platinum in so finely divided a state as it occurs in this ash inflames hydrogen, even at -20° . Many other metals, such as palladium (175°), iridium, and gold, act on a slight rise of temperature, like platinum; but mercury, at its boiling-point, does not inflame detonating gas, although the slow formation of water begins at 305° . All data of this kind show that the explosion of detonating gas forms one of the many cases of contact phenomena. This conclusion is further confirmed by the researches of V. Meyer (1892). He showed that only a very slow formation of steam begins at 448° , and that it only proceeds more rapidly at 518° . The temperature of the explosion of detonating gas, according to the same author, varies according to whether the explosion is produced in open vessels or in closed tubes. In the first case the temperature of explosion lies between 530° – 606° , and in the second between 630° – 730° . In general it may be remarked that the temperature of explosion of gaseous mixtures is always lower in closed vessels than when the detonating mixture flows freely through tubes. According to Freyer and V. Meyer, the following gases when mixed with the requisite amount of oxygen explode at the following temperatures:

—	When flowing freely	In closed vessels
H ₂ with oxygen	630° – 730°	530° – 606°
CH ₄ "	650° – 730°	606° – 650°
C ₂ H ₆ "	606° – 650°	530° – 606°
C ₂ H ₄ "	606° – 650°	530° – 606°
CO "	650° – 730°	650° – 730°
H ₂ S "	315° – 320°	250° – 270°
H ₂ + Cl ₂	430° – 440°	240° – 270°

Baker (1892) showed that perfectly pure detonating gas, prepared by the action of an electric current on a solution of caustic baryta (BaH₂O₂) and very carefully dried by volatilised phosphoric anhydride, does not give water or explode at those temperatures (even at 950°) at which moist detonating gas immediately forms water (compare Chap. IX., note 29). Besides which, Baker proved that the moist gas gradually gives water when exposed to sunlight, but that the dry gas does not react at all. In my opinion, all such instances are due to phenomena of contact; that is, in other words, they are determined by changes in the distribution of the atoms in the molecules which take place to a greater or less degree at all the planes of contact of different bodies. This is particularly clear in the above influence of metals.

The velocity of the transmission of explosion in gaseous mixtures is as characteristic a magnitude for gaseous systems as the velocity of the transmission of sound. Berthelot

eudiometer showed that the ignition of detonating gas takes place at a temperature between 450° and 560° .³⁶

showed that this velocity depends neither upon the pressure nor upon the size of the tubes in which the gaseous mixture is contained, nor upon the material of which the tube is made. Dixon (1891) determined the magnitude of these velocities for various mixtures, and his results agreed well with those previously given by Berthelot. For comparison we give the velocities expressed in metres per second:

	Dixon	Berthelot
$\text{H}_2 + \text{O}$	2,821	2,810
$\text{H}_2 + \text{N}_2\text{O}$	2,305	2,284
$\text{CH}_4 + 4\text{O}$	2,322	2,287
$\text{C}_2\text{H}_2 + 6\text{O}$	2,364	2,210
$\text{C}_2\text{H}_2 + 5\text{O}$	2,391	2,482
$\text{C}_2\text{N}_2 + 4\text{O}$	2,321	2,195

The addition of oxygen to detonating gas lowers the velocity of the transmission of explosion almost as much as the introduction of nitrogen. An excess of hydrogen, on the contrary, raises the velocity of transmission. It is remarked that the explosion of mixtures of oxygen with marsh gas, ethylene, and cyanogen is transmitted more quickly if the oxygen be taken in such a proportion that the carbon should burn to oxide of carbon, i.e., the velocity of the explosion is less if the oxygen be taken in sufficient quantity to form carbonic anhydride. Observations upon liquid and solid explosives (Berthelot) show that, in these cases, the velocity of transmission of explosion is dependent upon the material of the tube. Thus the explosion of liquid nitro-methyl ether in glass tubes travels at the rate (with variation of the diameter from 1 mm. to 45 mm.) of from 1,890 to 2,482 metres, and in tubes of Britannia metal (3 mm. in diameter) at the rate of 1,230 metres. The harder the tube the greater the velocity of transmission of explosion. The following are the velocities for certain bodies:

	metres per second
Nitro-glycerine	1,300
Dynamite	2,500
Nitro-mannite	7,700
Picric acid	6,500

In conclusion we may add that Mallard and Le Chatelier (1882) observed that in the explosion of a mixture of 1 volume of detonating gas with n volumes of an inert gas, the pressure is approximately equal to $9.20 - .9n$ atmospheres.

³⁶ From the very commencement of the promulgation of the idea of dissociation, it might have been imagined that reversible reactions of combination (the formation of H_2O from H_2 and O belongs to this class) commence at the same temperature as that at which dissociation begins. And in many cases this is so, but not always, as may be seen from the facts: (1) that at 450 – 560° , when detonating gas explodes, the density of aqueous vapour not only does not vary (and it hardly varies at higher temperatures, probably because the amount of the products of dissociation is small), but there are not, as far as is yet known, any traces of dissociation; (2) that under the influence of contact the temperature at which combination takes place falls even to the ordinary temperature, at which water and similar compounds are, of course, not dissociated; and, judging from the data communicated by D. P. Konovaloff (Introduction, note 39) and others, it is impossible to escape the phenomena of contact. All vessels, whether of metal or glass, show the same influence as spongy platinum, although to a much less degree. The phenomena of contact, judging from a review of the data referring to it, must be especially sensitive in reactions which are powerfully exothermic, and the explosion of detonating gas is of this kind.

The combination of hydrogen with oxygen is accompanied by the evolution of a very considerable amount of heat; according to the determinations of **Favre and Silbermann**,³⁷ 1 part by weight of hydrogen

³⁷ The amount of heat evolved in the combustion of a known weight (for instance, 1 gram) of a given substance is determined by the rise in temperature of a quantity of water, to which the whole of the heat evolved in the combustion is transmitted. A **calorimeter**, for example that shown in fig. 37, is employed for this purpose. It consists of a thin (in order that it may absorb less heat), polished (that it should transmit a minimum of heat) metallic vessel, surrounded by down (*c*), or some other bad conductor of heat, and an outer metallic vessel. This is necessary in order that the least possible amount of heat should be lost from the vessels; nevertheless, there is always a certain loss, the magnitude of which is determined by preliminary experiment (by taking warm water, and determining its fall in temperature after a definite period of time) as a correction for the results of observations. The water to which the heat of the burning substance

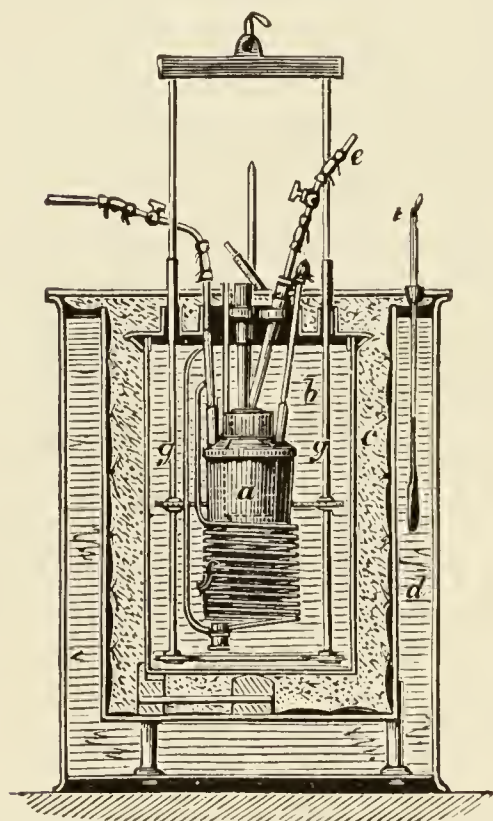


FIG. 37.—Favre and Silbermann's calorimeter for determining the heat evolved in combustion.

is transmitted is poured into the vessel. The stirrer *g* allows of all the layers of water being brought to the same temperature, which is determined by the thermometer. The heat evolved passes, naturally, not to the water only, but to all the parts of the apparatus. The quantity of water corresponding with the whole amount of those objects (the vessels, tubes, &c.) to which the heat is transmitted is previously determined, and in this manner another most important correction is made in the calorimetric determinations. The combustion itself is carried on in the vessel *a*. The ignited substance is introduced through the tube at the top, which closes tightly. In fig. 37 the apparatus is arranged for the combustion of a gas, introduced by a tube. The oxygen required for the combustion is led into *a* by the tube *e*, and the products of combustion either remain in the vessel *a* (if liquid or solid), or escape by the tube *f* into an apparatus in which their quantity and properties can easily be determined. Thus the heat evolved in combustion passes to the walls of the vessel *a*, and to the gases which are formed in it, and these transmit it to the water of the calorimeter.

The construction of the calorimeter and even the method of determination vary considerably in different cases. Since the beginning of the nineties, a large number of determinations of the heat of combustion have been conducted in closed bombs containing compressed oxygen. The greatest number of calorimetric determinations were made by Berthelot and by Thomsen. They are given in their works: *Essai de mécanique chimique fondée sur la thermochimie*, by M. Berthelot, 1879 (2 vols.), and *Thermochemische Untersuchungen*, by J. Thomsen, 1886 (4 vols.) The most important methods of recent thermochemistry, and all the trustworthy results of experiment, are given in Professor W. F. Louginin's *Description of the different Modes of determining the Heat of Combustion of Organic Compounds*, Moscow, 1894. The student must refer to works on theoretical and physical chemistry for a description of the elements and methods of **thermochemistry**, into the details of which it is impossible to enter in this work. One of the originators of thermochemistry, Hess, was a member of the St. Petersburg Academy of Sciences. Since 1870 a large amount of research has been carried out in this province of chemistry, especially in France and Germany, after the investigations of the French Academician, Berthelot, and Professor Thomsen, of Copenhagen. Among

in forming water evolves 34,462 units of heat. Many later determinations agree closely with this figure, so that it may be taken that in the formation of 18 parts of water (H_2O) there are evolved 69 major calories (each 1,000 times greater than the normal calorie, and therefore called kilogram-calories), or 69,000 units of heat.³⁸ *If the specific heat of aqueous vapour (0.48) remained constant from the ordinary temperature to that at which the combustion of detonating gas takes place* (and there is now no doubt that it increases rapidly, especially beyond $1,000^\circ$), were the combustion concentrated at one point³⁹ (but it occurs in the whole region of a flame), were there no loss from radiation and heat conduction, and *did dissociation* (which absorbs heat and consequently increases the apparent specific heat) *not take place*—that is, did not a state of equilibrium between the hydrogen, oxygen, and water come about—*then it would be possible to calculate the temperature of the flame of detonating gas.* It would then be $7,700^\circ$.⁴⁰ In reality it is

Russians, Beketoff, Werner, Louginin, Cheltzoff, Chroustchhoff, and others are known by their thermochemical researches. The present epoch of thermochemistry must be considered rather as a collective one, wherein the material of facts is being amassed, and the first consequences arising from them are being noticed. In my opinion two essential circumstances prevent the possibility of deducing any exact consequences, of importance to chemical mechanics, from the immense store of thermochemical data already collected: (1) The majority of the determinations are conducted in weak aqueous solutions, and, the heat of solution being known, are referred to the substances in solution; yet there is much (Chap. I.) which leads to the conclusion that water in solution does not play the simple part of a diluting medium, but of itself acts independently in a chemical sense on the substance dissolved. (2) Physical and mechanical changes (decrease of volume, diffusion, and others) invariably proceed side by side with chemical changes, and for the present it is impossible, in a number of cases, to distinguish the thermal effects of the one and the other kind of change. It is evident that the one kind of change (chemical) is essentially inseparable and incomprehensible without the other (mechanical and physical); and therefore it seems to me that thermochemical data will only acquire their true meaning when the connection between the phenomena of both kinds (on the one hand chemical and atomic, and on the other, mechanical and molecular or between entire masses) is explained more clearly and fully than is at present the case. As there is no doubt that the simple mechanical contact, or the action of heat alone, on substances sometimes causes an evident and always a latent (incipient) chemical change—that is, a different distribution or motion of the atoms in the molecules—it follows that purely chemical phenomena are inseparable from physical and mechanical phenomena. A mechanical change may be imagined without a physical change, and a physical without a chemical change; but it is impossible to imagine a chemical change without a physical and mechanical one, for without the latter we should not be able to recognise the former, and it is by their means that we are enabled to do so.

³⁸ This quantity of heat corresponds with the formation of water at the ordinary temperature from detonating gas at the same temperature. If the water be as vapour, the heat evolved is 58 major calories (because the latent heat of evaporation takes 600 calories per 1 part by weight of water, and there are 18 parts); if as ice, 70.4 major calories.

³⁹ This flame, or locality where the combustion of gases and vapours takes place, is a complex phenomenon, 'an entire factory,' as Faraday says, and therefore we will consider flame in some detail in one of the following notes.

⁴⁰ If 34,500 units of heat are evolved in the combustion of 1 part of hydrogen, and

very much lower, but it is nevertheless higher than the temperature

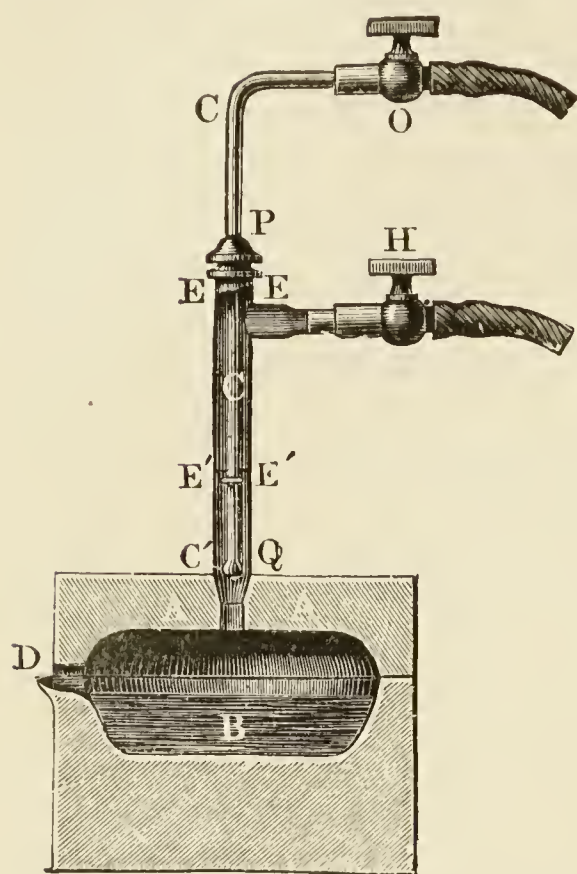


FIG. 38.—Safety burner for detonating gas, described in text.

attained in furnaces and flames, and is as high as $2,000^{\circ}$. The explosion of detonating gas is explained by this high temperature, because the aqueous vapour formed must occupy a volume at least five times greater than that occupied by the detonating gas at the ordinary temperature. Detonating gas emits a sound, not only as a consequence of the commotion which occurs from the rapid expansion of the heated vapour, but also because it is immediately followed by a cooling effect, the conversion of the vapour into water, and a rapid contraction.⁴¹

Mixtures of hydrogen and of various other combustible gases and vapours with oxygen are taken advantage of for obtaining high temperatures. By

the aid of such high temperatures, metals like platinum may be this heat is transmitted to the resulting 9 parts by weight of aqueous vapour, then we find that, taking the specific heat of the latter as 0.475 , each unit of heat raises the temperature of 1 part by weight of aqueous vapour 2.1° and 9 parts by weight ($2.1 \div 9$) 0.23° ; hence the $34,500$ units of heat raise its temperature $7,935^{\circ}$. If detonating gas is converted into water in a closed space, then the aqueous vapour formed cannot expand, and therefore, in calculating the temperature of combustion, the specific heat at constant volume must be taken into consideration; for aqueous vapour this is 0.36 . This figure gives a still higher temperature for the flame. In reality it is much lower, but the results given by different observers are very contradictory (from $1,700^{\circ}$ to $2,400^{\circ}$), the discrepancies depending on the fact that flames of different sizes are cooled by radiation to a different degree, but mainly on the fact that the methods and apparatus (pyrometers) for the determination of high temperatures, although they enable relative changes of temperature to be judged, are of little use for determining their absolute magnitudes. By taking the temperature of the flame of detonating gas as $2,000^{\circ}$, I give, I think, the average of the most trustworthy determinations and calculations based upon the determination of the variation of the specific heat of aqueous vapour and other gases.

The determination of the temperature of combustion or heating power (pyrometric effect, as it is often called) is considered more fully in speaking of combustion in my work, *The Principles of Industry. Fuel*, 1897, pp. 93–98. Why only $2,000^{\circ}$ is attained instead of $8,000^{\circ}$ is explained by the fact that between 0° and $2,500^{\circ}$ the *mean* apparent (combined with dissociation) specific heat of steam probably exceeds (judging from Mallard and Le Chatelier's observations, 1888) the specific heat of liquid water, and if the mean specific heat of steam be taken as about 1.9 , it is evident that only about $2,000^{\circ}$ will be obtained instead of $8,000^{\circ}$. Mallard and Le Chatelier showed that the mean specific heat of aqueous vapour up to the distinct commencement of dissociation may be taken as $0.4 + 0.0002t$. Dissociation is very considerable at the temperature of the flame of detonating gas, and this lowers the temperature or increases the apparent specific heat.

⁴¹ It is evident that not only hydrogen, but every other combustible gas and vapour, can

melted on a large scale, which cannot be performed in furnaces heated with charcoal and fed by a current of air of the ordinary temperature.^{41a} The burner shown in fig. 38 is constructed for the application of detonating gas to the purpose. It consists of two brass tubes, one fixed inside the other, as in the drawing. The inner central tube C C conducts the oxygen, and the outer, enveloping, tube, E' E', the hydrogen. Previous to their egress the gases do not mix together, so that there can be no explosion inside the apparatus. When the burner is in use, C is connected with a gas-holder containing oxygen, and E with a gasholder containing hydrogen (or sometimes coal-gas). The flow of the gases can be easily regulated by the stop-cocks O and H. The flame is shortest and evolves the greatest heat when the gases burning are in the proportion of 1 volume of oxygen to 2 volumes of hydrogen. The degree of heat may be easily judged from the fact that a thin platinum wire placed in the flame of a properly proportioned mixture readily melts. By placing the burner in the orifice of a hollow piece of lime, a crucible A B is obtained in which platinum may be readily melted, even in large quantities, if the current of oxygen and hydrogen be sufficiently great (Deville). The flame of detonating gas may also be used for illuminating purposes. By itself it is very pale, but owing to its high temperature, it serves for rendering infusible objects incandescent, and at the very high temperature produced by the detonating gas the incandescent substance gives a most intense light. For this purpose, lime, magnesia, or oxide of zirconium is used, as these are not fusible at the very high temperature generated by the detonating gas. A small cylinder of lime placed in the flame of detonating gas, if regulated to the required point, gives a very brilliant white light, which was at one time proposed for illuminating lighthouses. At present, in the majority

give an explosive mixture with oxygen. For this reason coal-gas mixed with air explodes when the mixture is ignited. The pressure obtained in the explosions serves as the **motive power of gas engines**. In this case advantage is taken, not only of the pressure produced by the explosion, but also of the contraction which takes place after the explosion. On this is based the construction of several motors, of which Lenoir's was formerly, and Otto's is now, the best known. The explosion is usually produced by coal-gas and air, but of late the vapours of combustible liquids (kerosene, benzine, naphtha) and the combustible gases of blast furnaces are also being employed (Chap. XXII.) In Lenoir's engine a mixture of coal-gas and air is ignited by means of sparks from a Ruhmkorff's coil; but in the most recent machines the gases are ignited by the direct action of a gas jet, or by contact with the hot walls of a side tube.

^{41a} However, if the air used for combustion be previously strongly heated, and charcoal or some combustible gas (lighting or generator, see Chap. IX., note 19) be burnt in it, then the melting-point of platinum (1,780°) and iron (1,450°) may be attained; and this is now taken advantage of in works in the so-called regenerator furnaces (see Chap. IX., note 19).

of cases, the electric light, owing to its constancy and other advantages, has replaced it for this purpose. The light produced by the incandescence of lime in detonating gas is called the **Drummond light** or **limelight**.

The above cases form examples of the combustion of elements in oxygen, but exactly similar phenomena are observed in the **combustion of compounds**. Thus, for instance, the solid, colourless, shiny substance, naphthalene, $C_{10}H_8$, burns in the air with a smoky flame, whilst in oxygen it continues to burn with a very brilliant flame. Alcohol, oil, and other substances burn brilliantly in oxygen on conducting the oxygen by a tube to the flames of lamps burning these substances. A high temperature is thus evolved, which is sometimes made practical use of in chemistry.

In order to understand why combustion in oxygen proceeds more rapidly, and is accompanied by a more intense heat effect, than combustion in air, it must be recollected that air is oxygen diluted with nitrogen, which does not support combustion, and therefore fewer particles of oxygen flow to the surface of a substance when burning in air than when burning in pure oxygen, and the heat evolved has, moreover, to heat the mass of nitrogen accompanying the oxygen as well as the products of combustion (and the oxygen).⁴²

⁴² Let us consider as an example the combustion of sulphur in air and in oxygen. If 1 gram of sulphur burns in air or oxygen it evolves in either case 2,250 units of heat, i.e., sufficient heat for heating 2,250 grams of water 1° C. This heat is first of all transmitted to the sulphurous anhydride, SO_2 , formed by the combination of sulphur with oxygen. In its combustion, 1 gram of sulphur forms 2 grams of sulphurous anhydride—i.e., 1 gram of the sulphur combines with 1 gram of oxygen. In order that 1 gram of sulphur should have access to 1 gram of oxygen in air, it is necessary that 3.4 grams of nitrogen should simultaneously reach the sulphur, because air contains 77 parts of nitrogen (by weight) per 23 parts of oxygen. Thus, in the combustion of 1 gram of sulphur, the 2,250 units of heat are transmitted to 2 grams of sulphurous anhydride and at least 3.4 grams of nitrogen. As 0.155 unit of heat is required to raise the temperature of 1 gram of sulphurous anhydride 1° C., 2 grams will require 0.31 unit. So also, 3.4 grams of nitrogen require 3.4×0.244 or 0.83 unit of heat, and therefore, in order to raise both gases 1° C., $0.31 + 0.83$ or 1.14 unit of heat is required; but as the combustion of the sulphur evolves 2,250 units of heat, the gases might be heated (if their specific heats remained constant) to $\frac{2250}{1.14}$ or $1,974^\circ$ C. That is, the

maximum possible temperature of the flame of sulphur burning in air will be $1,974^\circ$ C. In the combustion of the sulphur in oxygen the heat evolved (2,250 units) can only pass to the 2 grams of sulphurous anhydride, and therefore the highest possible temperature of the flame of sulphur in oxygen will be $= \frac{2250}{0.31}$ or $7,258^\circ$. This formation of

gaseous products in combustion must also lower the temperature of combustion. Therefore when a reaction takes place between solid bodies with the formation of solid bodies (or in general when the volume does not increase or varies but little, and all the more if contraction takes place), the heating effect may be very great. This is illustrated by a powdered mixture of molecular proportions of oxide of iron and metallic aluminium,

Among the phenomena accompanying the combustion of certain substances, the **phenomenon of flame** attracts attention. Sulphur, phosphorus, sodium, magnesium, naphthalene, &c. burn, like hydrogen, with a flame, whilst in the combustion of other substances no flame is observed, as, for instance, in the combustion of iron and of charcoal. The appearance of flame depends on the capacity of the combustible substance to yield gases or vapours at the temperature of combustion. At the temperature of combustion, sulphur, phosphorus, sodium, and naphthalene pass into vapour, whilst wood, alcohol, oil, &c. are decomposed into gaseous and vaporous substances. The combustion of gases and vapours forms flames, and therefore *a flame is composed of the hot incandescent gases and vapours produced by combustion*. It may easily be proved, by placing a tube in the flame connected with an aspirator, that the flames of such non-volatile substances as wood contain volatile and combustible substances formed from them. Besides the products of combustion, combustible gases and liquids, previously in the flame as vapours, collect in the aspirator. For this experiment to succeed—i.e., in order to really extract combustible gases and vapours from the flame—it is necessary that the suction tube should be placed *inside* the flame. The combustible gases and vapours can only remain unburnt inside the flame, for at its surface they come into contact with the oxygen of the air and burn.^{42a} Flames are of different degrees of **brilliancy**, according to whether *solid* incandescent particles occur in the combustible gas or vapour, or not. Incandescent gases and vapours emit but little light by themselves, and therefore give a paler flame.⁴³ If a flame does not contain solid particles it is transparent, pale, and emits but little light.⁴⁴ The flames of burning

Goldschmidt's thermite, which after ignition (by a magnesium wire bent into the mixture) burns and gives a temperature as high as $3,000^{\circ}$ (according to the equation $\text{Fe}_2\text{O}_3 + \text{Al}_2 = \text{Al}_2\text{O}_3 + \text{Fe}_2$) at which the resultant iron melts. The temperature is undoubtedly higher than in the hydrogen flame.

^{42a} Faraday proved this by a very convincing experiment on a candle flame. If one arm of a bent glass tube be placed in a candle flame in the dark portion of the flame above the wick, then the products of the partial combustion of the stearin will pass up the tube, condense in the other arm, and collect in a flask placed under it (fig. 39) as heavy white fumes which burn when lighted. If the tube be raised into the upper luminous portion of the flame, a dense black smoke which will not inflame accumulates in the flask. Lastly, if the tube be let down until it touches the wick, little but stearic acid condenses in the flask.

⁴³ All transparent substances which transmit light with great ease (that is, which absorb but little light) are but slightly luminous when heated; so also substances which absorb but few heat rays, when heated, transmit few rays of heat.

⁴⁴ There is, however, no doubt but that very heavy dense vapours or gases under pressure (according to the experiments of Frankland) are luminous when heated, because, as they become denser, they approach a liquid or solid state. Thus, detonating gas, when exploded under pressure, gives a brilliant light.

alcohol, sulphur, and hydrogen are of this kind. A pale flame may be rendered luminous by placing fine particles of solid matter in it. Thus, if a very fine platinum wire be placed in the pale flame of burning alcohol—or, better still, of hydrogen—the flame emits a bright light.

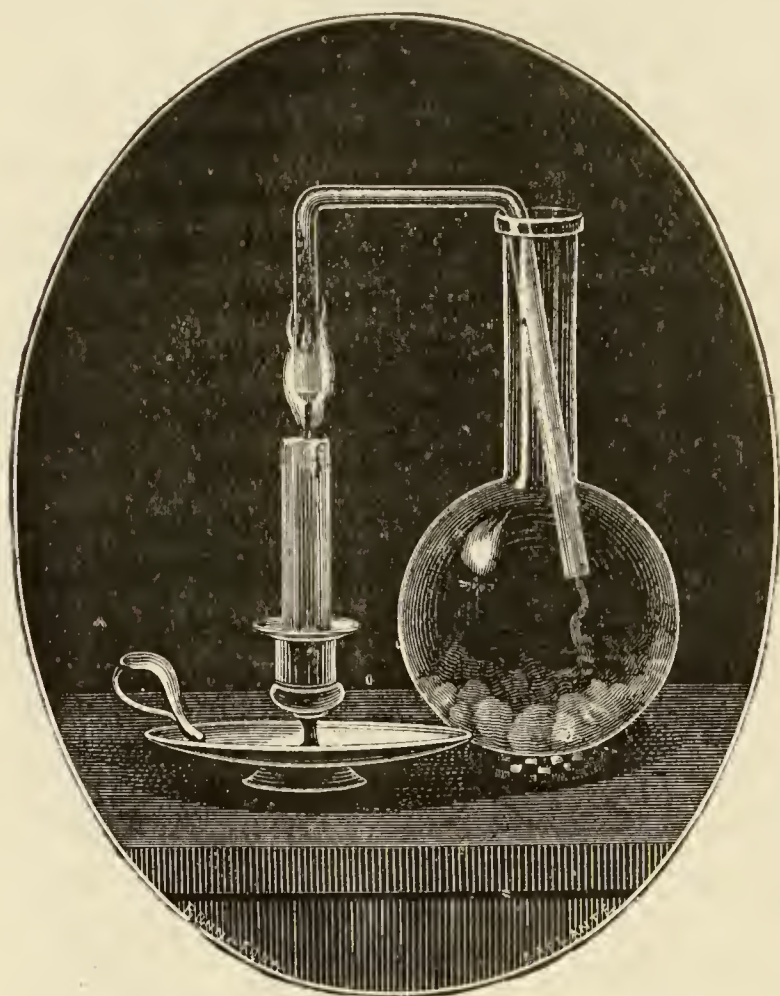


FIG. 39.—Faraday's experiment for investigating the different parts of a candle flame.

This is still better seen by sifting the powder of an incombustible substance, such as fine sand, into the flame, or by placing a bunch of asbestos threads in it. A brilliant flame always contains some kind of solid particles, or at least some very dense vapour. The flame of sodium burning in oxygen has a brilliant yellow colour, from the presence of particles of solid sodium oxide. The flame of magnesium is brilliant from the fact that, in burning, it forms solid magnesia, which becomes white hot, and similarly the brilliancy of the Drummond light is

due to the heat of the flame raising the lime to a state of incandescence. The flames of a candle, wood, and similar substances are brilliant, because they contain particles of charcoal or soot. It is not the flame itself which is luminous, but the incandescent soot it contains. These particles of charcoal which occur in flames may be easily observed by introducing a cold object, like a knife, into the flame.⁴⁵ The particles of charcoal burn at the outer surface of the flame if the supply of air is sufficient; but if the supply of air—that is, of oxygen—be insufficient for their combustion the flame will smoke, because the

⁴⁵ If hydrogen gas be passed through a volatile liquid hydrocarbon—for instance, through benzine (the benzine may be poured directly into the vessel in which the hydrogen is generated)—its vapour then burns with the hydrogen and gives a very bright flame, because the resultant particles of carbon (soot) become incandescent. Benzine or platinum gauze, introduced into a hydrogen flame, may be employed for illuminating purposes. The smoke of stoves, owing to imperfect combustion (due to various causes, especially to the imperfect mixture of the products of combustion with air and a local fall of temperature) of the fuel, frequently contains soot. This could not occur unless the soot had been previously formed in the flame.

unconsumed particles of charcoal are carried off by the current of air.⁴⁶

⁴⁶ In **flames**, the separate parts may be distinguished]with more or less distinctness. That portion of the flame to which the combustible vapours or gases flow is not luminous because its temperature is still too low for the process of combustion to take place in it. This is the space which in a candle surrounds the wick, or in a gas jet is immediately above the orifice from which the gas escapes. In a candle, the combustible vapours and gases formed by the action of heat on the melted tallow or stearin, rise in the wick and are heated by the high temperature of the flame. By the action of the heat, the solid or liquid substance is here, as in other cases, decomposed, forming products of dry distillation, and these products occur in the central portion of the flame of a candle. The air travels to it from the outside, and is not able to intermix equally with the vapours and gases in all parts of the flame at once; consequently in the outer portion of the flame the amount of oxygen will be greater than in the interior portions. But, owing to diffusion, the oxygen, of course mixed with nitrogen, flowing towards the combustible substance, does finally penetrate to the interior of the flame (when the combustion takes place in ordinary air). The combustible vapours and gases combine with this oxygen, evolve a considerable amount of heat, and bring about that state of incandescence which is so necessary both for keeping up the combustion and also for the uses to which the flame is applied. Passing from the colder envelope of air through the interior of the flame to the source of the combustible vapours (for instance, the wick), we evidently first traverse layers of higher and higher temperature, and then portions which are less and less hot, in which the combustion is less complete, owing to the limited supply of oxygen.

Thus, unburnt products of the decomposition of organic substances occur in the interior of the flame. But there is always free hydrogen in the interior of the flame, even when oxygen is introduced there, or when a mixture of hydrogen and oxygen burns, because the temperature evolved in the combustion of hydrogen or the carbon of organic matter is so high that the products of combustion are themselves partially decomposed—that is, dissociated—at this temperature. Hence, in a flame a portion of the hydrogen and of the oxygen which might combine with the combustible substances must always be present in a free state. If a hydrocarbon burns, and we imagine that a portion of the hydrogen is in a free state, then a portion of the carbon must also occur in the same form in the flame, because, other conditions being unchanged, carbon burns after hydrogen, and this is actually observed in the combustion of various hydrocarbons. Charcoal, or the soot of a common flame, arises from the dissociation of organic substances contained in the flame. The majority of hydrocarbons, especially those containing much carbon—for instance, naphthalene—burn, even in oxygen, with separation of soot. In that portion of the flame where the hydrogen burns, the carbon remains unburnt, or at least partly so. That the interior of the flame contains a mixture which is still capable of combustion may be proved by the following experiment. A portion of the gases may be withdrawn by an aspirator from the central portion of the flame of carbonic oxide, which is combustible in air. For this purpose Deville passed water through a metallic tube, having a fine lateral orifice, placed in the flame. As the water flows along the tube, portions of the gases of

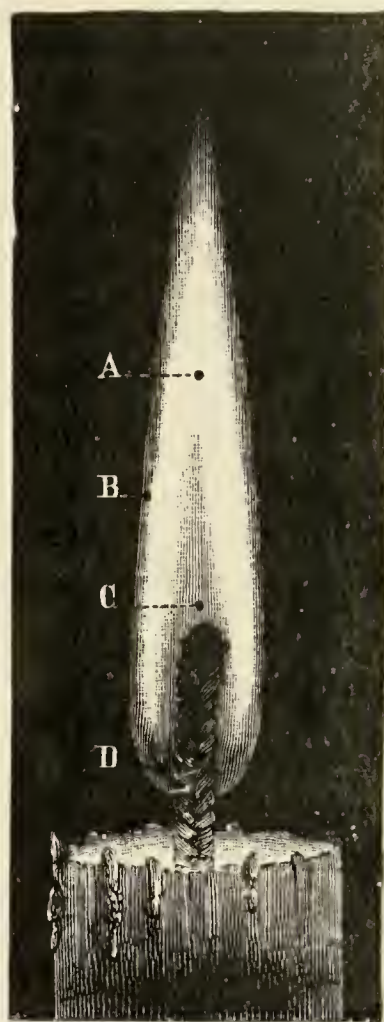


FIG. 40.—In the candle flame the portion C contains the vapours and products of decomposition; in the bright zone A the combustion has commenced, and particles of carbon are emitted; and in the pale zone B the combustion is completed.

The combination of various substances with oxygen may not present any signs of combustion—that is, the temperature may rise but inconsiderably. This may proceed from the fact that either the reaction of the substance (for example, tin, mercury, lead at a high temperature, or a mixture of pyrogallol with caustic potash at the ordinary temperature) evolves but little heat, or the heat evolved is transmitted to good conductors of heat, like metals, and so dispersed, or combination with oxygen takes place so slowly that the heat evolved succeeds in gradually passing to the surrounding objects. Combustion is only a particular, intense, and evident case of combination with oxygen. Respiration is also an act of combination with oxygen: it also serves, like combustion, for the development of heat by those chemical processes which accompany it (the transformation of

the flame enter, and, passing along the tube alternately with small cylinders of water, are carried away into an apparatus where they can be investigated. It appears that all portions of the flame obtained by the combustion of a mixture of carbonic oxide and oxygen contain a portion of this mixture still unburnt. The researches of Deville and Bunsen showed that in the explosion of a mixture of hydrogen or of carbonic oxide with oxygen in a closed space, complete combustion never takes place immediately. If two volumes of hydrogen and one volume of oxygen be confined in a closed space and exploded, the pressure will not attain that magnitude which it would do, were there immediate and complete combustion. It may be calculated that the pressure should attain 20–30 atmospheres; but in reality it does not exceed $9\frac{1}{2}$ atmospheres.

Hence the admixture of the products of combustion with an explosive mixture prevents the combustion of the remaining mass, although this is capable of burning. Admixture of carbonic anhydride prevents carbonic oxide from burning. The presence of any other foreign gas interferes in the same manner. This indicates that every portion of a flame must contain combustible, burning, and already burnt substances—i.e., oxygen, carbon, carbonic oxide, hydrogen, hydrocarbons, carbonic anhydride, and water—in one place. Consequently **it is impossible to attain instantaneous complete combustion**, and this is one of the reasons of the phenomenon of flame. A certain space is required, and the temperature must be unequal in different parts of it. In this space different quantities of the component parts are successively subjected to combustion, and to partial cooling under the influence of adjacent objects. If the combustion could be concentrated at one spot, the temperature would be incomparably higher than it is under the actual circumstances.

The various regions of the flame have frequently formed the subject of experimental research, and the experiments conducted by Smithells and Ingle (1892) are particularly instructive: they show that the reducing (inner) and oxidising (outer) portions of the flame of a burning gas may be separated by taking a Bunsen burner and surrounding the flame of the gas burnt in it by another wider tube (either without the access of air to the annular space or allowing only a small current of air to pass), when a gaseous mixture, containing oxide of carbon and capable of further combustion, will issue from this enveloping tube, so that a second flame, corresponding to the exterior (oxidising) portion of an ordinary flame, may be obtained above the enveloping tube. This division of the flame into two portions is particularly clear when cyanogen, C_2N_2 , is burnt, because the interior portion (where CO is chiefly formed, according to the equation, $C_2N_2 + O_2 = 2CO + N_2$, but a portion of the nitrogen is oxidised) is of a rose colour, while the exterior portion (where the CO burns into CO_2 at the expense of a fresh quantity of oxygen and of the oxides of nitrogen proceeding from the interior portions) is of a bluish-grey colour.

oxygen into carbonic anhydride). Lavoisier enunciated this in the lucid expression, 'Respiration is slow combustion.'

Reactions involving slow combination of substances with oxygen are termed **oxidations**. Combination of this kind (and also combustion) often results in the formation of acid substances, and hence the name **oxygen** (*Sauerstoff*). Combustion is only rapid oxidation. Phosphorus, iron, and wine may be taken as examples of substances which oxidise slowly in air at the ordinary temperature. If such a substance is left in contact with a definite volume of air or oxygen, it will absorb the oxygen little by little. This slow oxidation is not often accompanied by a sensible evolution of heat; an evolution of heat really does occur, but is not apparent to our senses owing to the small rise in temperature which takes place; this is due to the slow rate of the reaction and to the dispersion of the heat formed as radiant heat, &c. Thus, in the oxidation of wine and its transformation into vinegar by the usual method of preparation of the latter, the heat evolved cannot be observed, because the process extends over several weeks; but in the so-called rapid process of the manufacture of vinegar, when a large quantity of wine is comparatively rapidly oxidised, the evolution of heat is quite apparent.

Such slow processes of oxidation are always taking place in nature by the action of the atmosphere. Dead organisms and the substances obtained from them—such as bodies of animals, wood, wool, grass, &c.—are especially subject to this action. They **rot** and **decompose**—that is, their solid matter is gradually transformed, completely or partially, into gases, under the influence of moisture and atmospheric oxygen, and generally under the influence of other organisms, such as moulds, worms, micro-organisms (bacteria), and the like. These are processes of slow combustion, of slow combination with oxygen. It is well known that manure rots and develops heat and that stacks of damp hay, damp flour, straw, &c., become heated and are changed in the process.⁴⁷ In all these transformations the same chief products of combustion are formed as those which are contained in smoke: the carbon gives carbonic anhydride, and the hydrogen, water. Hence these processes require oxygen just like combustion. This is the reason why the entire prevention of access of air hinders these transformations⁴⁸ and an

⁴⁷ Cotton waste (used in factories for cleaning machines from lubricating oil), soaked in oil and lying in heaps, is self-combustible, being oxidised by the air. In general, the oxidation of combustible bodies (for instance, of coal containing pyrites undergoing oxidation) may produce spontaneous combustion.

⁴⁸ When it is desired to preserve a supply of vegetable and animal food, the access of the oxygen of the atmosphere (and also of the germs of organisms present in the air) is often prevented. With this object, articles of food are often kept in hermetically closed

increased supply of air accelerates them. The mechanical treatment of arable lands by the plough, harrow, and other similar means has not only the object of facilitating the spread of roots in the ground, and of making the soil more permeable to water, but it also serves to facilitate the access of the air to the component parts of the soil, as a consequence of which the organic remains of soil rot—as it were, breathe air and evolve carbonic anhydride. One acre of good garden land, in the course of a summer, evolves more than sixteen tons of carbonic anhydride.

It is not only vegetable and animal substances which are subject to slow oxidation in the presence of water and air. Some metals rust under these conditions. Many metallic sulphides (for example, pyrites) are very easily oxidised with access of air and moisture. So that processes of slow oxidation proceed throughout nature. However, there are many elements which do not, under any circumstances, combine directly with gaseous oxygen; nevertheless, their compounds with oxygen may be obtained. Platinum, gold, iridium, chlorine, and iodine are examples of such elements. In this case recourse is had to a so-called **indirect method of oxidation**—i.e., the given substance is combined with another element, and by a method of double decomposition, this element is replaced by oxygen. The oxides so formed often readily lose their oxygen. Such, for example,* are the compounds of oxygen with chlorine, nitrogen, and platinum, which evolve oxygen on heating, so that they may be used as oxidising agents. In this respect **oxidising agents**, or those compounds of oxygen which are employed in chemical and technical practice for transferring oxygen to other substances, are especially noteworthy. The most important among these is nitric acid or **aqua fortis**, which is rich in oxygen and capable of evolving it when heated, and easily oxidises a great number of substances. Thus, nearly all metals and organic substances containing carbon and hydrogen are more or less oxidised when heated with nitric acid. If strong nitric acid be taken, and a piece of burning charcoal be immersed in the acid, it continues to burn. Chromic acid acts like nitric acid, alcohol burning when mixed with it. Although the action is not so marked, even water may oxidise with its oxygen. Sodium is not oxidised in perfectly dry oxygen at the ordinary tem-

vessels, from which the air has been withdrawn; vegetables are dried and soldered up, while hot, in tin boxes; sardines are immersed in oil, &c. The removal of water from substances is also sometimes resorted to with the same object (the drying of hay, corn, fruits), as also is saturation with substances which absorb oxygen (such as sulphurous anhydride) or which hinder the growth of organisms forming the first cause of putrefaction, as in processes of smoking, embalming, and in the keeping of fishes and other animal specimens in spirit, &c.

perature, but it burns very easily in water and aqueous vapour. Charcoal can burn in carbonic anhydride—a product of combustion—forming carbonic oxide. Magnesium burns in the same gas, separating carbon from it. Speaking generally, combined oxygen can pass from one compound to another.

The products of combustion or oxidation—and in general the definite compounds of oxygen—are termed **oxides**. Some oxides are not capable of combining with other oxides—or combine with only a few, and then with the evolution of very little heat; others, on the contrary, easily enter into combination with many other oxides, and in general possess remarkable chemical activity. This difference, however, is not well defined, and will become clearer as we become acquainted with the various oxides.

The class of oxides capable of entering into mutual combination we will term **saline oxides**. They fall into two chief groups—at least as regards the most extreme members. The members of one group combine with the members of the other group with particular ease. As representative of one group may be taken the oxides of the metals, magnesium, sodium, calcium, &c. Representatives of the other group are the oxides formed by the non-metals, sulphur, phosphorus, carbon. Thus, if we take the oxide of calcium, or lime, and bring it into contact with oxides of the second group, combination very readily ensues with the evolution of heat. For instance, if we mix calcium oxide with oxide of phosphorus they form phosphate of lime. If we pass the vapour of sulphuric anhydride, obtained by the combination of sulphurous oxide with oxygen, over pieces of lime heated to redness, the sulphuric anhydride is absorbed by the lime with the formation of a substance called ‘calcium sulphate.’ The oxides of the first kind, which contain metals, are termed **basic oxides** or **bases**. Lime is a familiar example of this class. The oxides of the second group, which are capable of combining with the bases, are termed **anhydrides of the acids** or **acid oxides**. Sulphuric anhydride, SO_3 , may be taken as a type of the latter group. It is a compound of sulphur with oxygen, formed not directly, but by the addition of a fresh quantity of oxygen to sulphurous anhydride, SO_2 , by passing it together with oxygen over incandescent spongy platinum. Carbonic anhydride, phosphoric anhydride, sulphurous anhydride, are all acid oxides.

If a given element forms but one basic oxide, it is termed the **oxide**; for example, calcium oxide, magnesium oxide, potassium oxide. Some indifferent oxides are also called ‘oxides,’ if they have not the properties of peroxides and at the same time do not show the properties of acid anhydrides; for example, carbonic oxide, of which mention has already

been made. If an element forms two basic oxides (or two indifferent oxides not having the characteristics of a peroxide), that of the lower degree of oxidation is called a **suboxide**—that is, suboxides contain less oxygen than oxides. Thus, when copper is heated to redness in a furnace, it increases in weight and absorbs oxygen, until for 63 parts of copper there is absorbed not more than 8 parts of oxygen by weight, forming a red mass, which is suboxide of copper, Cu_2O ; but if the roasting be prolonged, and the draught of air increased, 63 parts of copper absorb 16 parts of oxygen, and form black oxide of copper, CuO . Sometimes, to distinguish between the degrees of oxidation, a change of suffix is made in the oxidised element, **-ic** oxide denoting the higher degree of oxidation, and **-ous** oxide the lower degree. Thus ferrous oxide, FeO , and ferric oxide, Fe_2O_3 , are the same as suboxide of iron and oxide of iron. If an element forms one acid anhydride only, it is then named by an adjective formed from the name of the element made to end in **-ic** and the word **anhydride**. When an element forms two anhydrides, then the suffixes **-ous** and **-ic** are used to distinguish them, **-ous** signifying less oxygen than **-ic**; for example, sulphurous and sulphuric anhydrides.⁴⁹ When several oxides are formed from the same

⁴⁹ It must be remarked that certain elements form oxides of both chief kinds—i.e., basic and acid; for example, manganese forms the basic oxides: manganous oxide and manganic oxide, and the acid oxides: red oxide of manganese and manganic anhydride. Between them stands the dioxide (or peroxide) which was mentioned above and is a feeble base and a feeble acid anhydride. The basic oxides contain less oxygen than the peroxides, and the peroxides less than the acid anhydrides. The majority of elements, however, do not give all three kinds of oxides, some giving only one degree of oxidation. It must further be remarked that there are oxides formed by the combination of acid anhydrides with basic oxides, or, in general, of oxides with oxides. For every oxide having a higher and a lower degree of oxidation, it might be said that the intermediate oxide was formed by the combination of the higher with the lower oxide. But this is not true in all cases—for instance, when the oxide under consideration forms a whole series of independent compounds—for oxides which are really formed by the combination of two other oxides do not give such independent compounds, but in many cases decompose into the higher and lower oxides. As the intensity of the basic and acid properties varies considerably in different oxides, and some oxides combine (form salts) both with powerful bases and with strong acids, the nomenclature of the oxides, based on their salt-forming capacity, is more or less conventional and founded on historical tradition. Therefore, it is now often customary to name the oxides after the number of atoms of oxygen they contain; for instance, SO_2 , dioxide of sulphur; SO_3 , trioxide of sulphur; MnO , monoxide of manganese; Mn_2O_3 , sesquioxide of manganese; MnO_2 , dioxide of manganese, &c. But this method has the disadvantage of ignoring the qualities of the oxides, which are historically of primary importance in chemistry. Therefore (for science not founded on history is absurd), in this work, the *quantitative* nomenclature is only had recourse to where the oxides do not possess distinctly basic, acid, or peroxide properties; for example, MnO_2 and PbO_2 are better named dioxides than peroxides, as the latter (see Chapter IV.) are assumed to possess a special series of particular properties. A nomenclature, like a language, must always be a matter of conventional agreement. The propagation of knowledge depends largely upon it; but the substance and essence of knowledge do not, for language is a means and not an end

element, the prefixes **mono-**, **di-**, **tri-**, **tetra-**, are used, thus; chlorine monoxide, chlorine dioxide, chlorine trioxide, and chlorine tetroxide or chloric anhydride.

The majority of, if not all, basic and acid oxides combine with water, either by a direct or an indirect method, forming **hydrates**, that is, compounds which split up only into water and an oxide. It is well known that many substances are capable of combining with water. Oxides possess this property in the highest degree. We have already seen examples of this (Chapter I.) in the combination of lime, and of sulphuric and phosphoric anhydrides, with water. The resulting combinations are basic and acid hydrates. Acid hydrates are called **acids** because they have an acid taste when dissolved in water (or saliva), for then only can they act on the palate. Vinegar, for example, has an acid taste because it contains acetic acid dissolved in water. Sulphuric acid, H_2SO_4 , to which we have frequently referred, because it is the acid of the greatest importance both in practical chemistry and for its technical applications, is really a hydrate formed by the combination of sulphuric anhydride, SO_3 , with water, H_2O . Besides their acid taste, dissolved acids or acid hydrates have the property of changing the blue colour of certain vegetable dyes to red. Of these dyes **litmus** is especially noticeable and is much used. It is the blue substance extracted from certain lichens, and is used for dyeing tissues blue: it gives a blue infusion with water. This infusion, on the addition of an acid, **changes from blue to red.**⁵⁰

⁵⁰ Blotting or unsized paper, soaked in a solution of litmus, is usually employed for detecting the presence of acids. This paper is cut into strips, and is called *test paper*; when dipped into acid it turns red. This is a most sensitive reaction, and may be employed for testing for the smallest traces of acids. If 10,000 parts by weight of water be mixed with 1 part of sulphuric acid, the coloration is distinct, and it is even perceptible on the addition of ten times more water. Certain precautions must, however, be taken in the preparation of such very sensitive litmus paper. Litmus is sold in lumps. Take, say, 100 grams of it; powder it, and add it to pure cold water in a flask; shake and decant the water. Repeat this three times. This is done to wash away easily soluble impurities, especially alkalies. Transfer the washed litmus (it is washed with absolute alcohol to remove the non-sensitive reddish colouring matter) to a flask, and pour in 600 c.c. of water, heat, and allow the hot infusion to remain for some hours in a warm place. Then filter, and divide the filtrate into two parts. Add a few drops of nitric acid to one portion, so that a faint red tinge is obtained, and then mix the two portions. Add spirit to the mixture, and keep it in a stoppered bottle (it soon spoils if left open to the air). This infusion may be employed directly; it reddens in the presence of acids, and turns blue in the presence of alkalis. If evaporated, a solid mass is obtained which is soluble in water, and may be kept unchanged for any length of time. The test paper may be prepared as follows:—Take a strong infusion of litmus and soak blotting-paper with it; dry the latter and cut it into strips, and use it as test paper for acids. For the detection of alkalis, the paper must be soaked in a solution of litmus just reddened by a few drops of acid; if too much acid be taken, the paper will not be sensitive. Such acids as sulphuric acid colour litmus, and especially its infusion, a brick-red colour, whilst more feeble acids,

Basic oxides, in combining with water, form hydrates, of which, however, very few are soluble in water. Those which are soluble in water have an alkaline taste like that of soap or of water in which wood ashes have been boiled, and are called **alkalies**. Alkalies have the property of restoring the blue colour to litmus which has been reddened by the action of acids. The hydrates of the oxides of sodium and potassium, NaHO and KHO , are examples of basic hydrates easily soluble in water. They are true alkalis, and are termed **caustic**, because they act very powerfully on the tissues of animals and plants. Thus NaHO is called 'caustic' soda.

The saline oxides are capable of combining together and with water. Water itself is an oxide, and not an indifferent one, for it can, as we have seen, combine with basic and acid oxides: it is a representative of a whole series of saline oxides, **intermediate oxides**, capable of combining with both basic and acid oxides. There are many such oxides, which, like water, combine with basic and acid anhydrides; for

such as carbonic, give a faint wine-red tinge. Test paper of a yellow colour is also employed: it is dyed by an infusion of turmeric roots in spirit. In alkalis it turns brown, but regains its original hue in acids. Many blue and other vegetable colouring matters may be used for the detection of acids and alkalis; for example, infusions of cochineal, violets, logwood, &c. Certain artificially prepared substances and dyes may also be employed. Thus rosolic acid, $\text{C}_{20}\text{H}_{16}\text{O}_8$, and phenolphthaleïn, $\text{C}_{20}\text{H}_{14}\text{O}_4$ (which is used in an alcoholic solution, and is not suitable for the detection of ammonia), are colourless in an acid, and red in an alkaline, solution. Cyanine is also colourless in the presence of acids, and gives a blue coloration with alkalis. Methyl-orange (yellow in an aqueous solution) is not altered by alkalis, but becomes pink with acids (weak acids have no action), &c. These are very sensitive tests. Their behaviour in respect to various acids, alkalis, and salts sometimes gives the means of distinguishing substances from each other, and even for distinguishing different stages of combination between bases and acids; but we will not enter upon the details of this subject, because it chiefly concerns certain portions of analytical chemistry.

However certain peculiarities of these two reagents, phenolphthaleïn and methyl-orange, deserve our attention, all the more as they may both be obtained in a perfectly chemically pure form exhibiting their peculiarities, and they were recommended by a special committee of the Paris Congress of Chemists in 1900. The former (phenolphthaleïn) reacts equally well with feeble and strong acids; whilst methyl-orange (otherwise known as helianthine) only reacts with strong mineral acids (H_2SO_4 , HCl , &c.), and is not acted upon by such feeble acids as carbonic, salicylic, &c. (which is often very convenient). The transition from the reddish acid solution to the colourless (from the addition of alkalis) and back is so distinct with phenolphthaleïn that it forms one of the most sensitive reagents. Methyl-orange is less sensitive, especially under artificial (yellow) illumination.

Attention must also be drawn to the fact that in calling a solution neutral, acid, or basic, according to the change of colour of litmus paper, it is necessary to add (or understand) 'with regard to litmus,' as other reagents may give other results. Here, again, as in the case of distinguishing bases from acids, or neutral salts from acid salts, &c., there is a certain conventionalism of speech or expression which it is very difficult to avoid, but which has very little significance to the science itself, although apparently important to the beginner. In such cases the student is advised, like Arago, to go on further, and the details will become gradually clear of themselves.

instance, the oxides of aluminium and tin, &c. From this it may be concluded that all oxides might be placed, in respect to their capacity for combining with one another, in one uninterrupted series, at one extremity of which would stand those oxides which do not combine with the bases—that is, the alkalis—while at the other end would be the acid oxides, and in between, those oxides which combine with one another and with both the acid and basic oxides. The further apart the members of this series are, the more stable are the compounds they form together, the more energetically do they act on each other, the greater as a rule the quantity of heat evolved in their reaction, and the more marked is their saline chemical character.

Although basic and acid oxides combine together, they rarely react on each other; this depends on the fact that the majority of them are solids or gases—that is, they occur in the state least prone to chemical reaction. The gaseo-elastic state is with difficulty destroyed, because it necessitates overcoming the elasticity proper to the gaseous particles. But the solid state is characterised by the immobility of its particles, whilst chemical action requires contact and hence a displacement and mobility. If solid oxides be heated, and especially if they be melted, reaction proceeds with great ease. But such a change of state rarely occurs in nature or in practice. For example, in the manufacture of glass, the oxides contained in it are combined together in a molten mass. But when oxides combine with water, and especially when they form hydrates soluble in water, the mobility of their particles increases to a considerable extent, and their interaction is greatly facilitated. Reaction then often takes place at the ordinary temperature—easily and rapidly; so that this kind of reaction belongs to the class of those which take place with unusual facility, and are, therefore, very often taken advantage of in practice, and are going on in nature at every step. We will now consider the reactions of oxides in the state of hydrates, not losing sight of the fact that water is itself an oxide with definite properties, and has, therefore, no little influence on the course of those changes in which it takes part.

If we take a definite quantity of an acid, and add an infusion of litmus to it, it turns red; the addition of an alkaline solution does not immediately alter the red colour of the litmus, but on adding more and more of the alkaline solution a point is reached when the red colour changes to violet, and then the further addition of a fresh quantity of the alkaline solution changes the colour to blue. This change of the colour of the litmus is a consequence of the formation of a new compound. This reaction is termed the **saturation** or **neutralisation** of the acid by the base, or *vice versâ*. The solution in which the acid

properties of the acid are saturated by the alkaline properties of the base is termed a **neutral** solution. Such a solution, although derived from the mixture of a base with an acid, does not exhibit either an acid or basic reaction towards litmus; yet it preserves many other signs of the acid and alkali. What takes place is essentially the same as in the formation of water from hydrogen and oxygen. It is observed that in such a definite admixture of an acid with an alkali, besides the changes in the colour of litmus there is a heating effect—i.e., an evolution of heat—which is alone sufficient to prove that there was chemical action. And, indeed, if the resultant violet solution be evaporated, there separates out, not the acid or the alkali originally taken, but a substance which has neither acid nor alkaline properties, but is usually solid and crystalline, having a saline appearance: this is a **salt** in the chemical sense of the word. Hence a salt is derived from the reaction of an acid on an alkali, in a certain definite proportion. The water here taken for solution plays no part other than that of a medium, facilitating the progress of the reaction. This is seen from the fact that the anhydrides of the acids are able to combine with basic oxides, and give the same salts as do the acids with the alkalis or hydrates. Hence, a salt is a compound of definite quantities of an acid and an alkali. In the latter reaction, water is separated out if the substance formed is the same as is produced by the combination of anhydrous oxides together.⁵¹ Examples of the formation of salts from acids and bases are easily observed, and are very often applied in practice. If we take, for instance, insoluble magnesium oxide (magnesia), it is easily dissolved in sulphuric acid, and on evaporation gives a saline substance, bitter, like all the salts of magnesium, and familiar to all under the name of Epsom salts, which is used as a purgative. If a solution of caustic soda—which is obtained, as we saw, by the action of water on sodium oxide—be poured into a flask in which charcoal has been burnt; or if carbonic anhydride, which is produced under so many circumstances, be passed through a solution of caustic soda, sodium carbonate or soda, Na_2CO_3 , of which we have spoken several times, and which is prepared on a large scale and often used in manufactures, is obtained. This reaction

⁵¹ That water really is separated in the reaction of acid on alkaline hydrates may be shown by taking some other intermediate hydrate—for example, alumina—instead of water. Thus, if a solution of alumina in sulphuric acid be taken, it will have, like the acid, an acid reaction, and will therefore colour litmus red. If, on the other hand, a solution of alumina in an alkali—say potash—be taken, it will have an alkaline reaction, and will turn red litmus blue. On adding the alkaline to the acid solution until neither an alkaline nor an acid reaction is produced, a salt is formed, consisting of sulphuric anhydride and potassium oxide. In this, as in the reaction of hydrates, an intermediate oxide is separated out—namely, alumina. Its separation will be very evident in this case, as alumina is insoluble in water.

is expressed by the equation, $2\text{NaHO} + \text{CO}_2 = \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$. Thus, the various bases and acids form an innumerable number of different salts.⁵² Salts constitute an example of definite chemical compounds, and both in the history and practice of science are most often cited as confirming the conception of definite chemical compounds. Indeed, all the indications of a definite chemical combination are clearly seen in the formation and properties of salts. Thus, they are produced from definite proportions of oxides, heat is evolved in their formation,⁵³ and

⁵² The mutual interaction of hydrates, and their capacity of forming salts, may be taken advantage of for determining the character of those hydrates which are insoluble in water. Let us imagine that a given hydrate, whose chemical character is unknown, is insoluble in water, so that it is impossible to test its reaction on litmus. It is then mixed with water, and an acid—for instance, sulphuric acid—is added to the mixture. If the hydrate taken be basic, reaction will take place, either directly or on heating, with the formation of a salt. In certain cases, the resultant salt is soluble in water, and this will at once show that combination has taken place between the insoluble basic hydrate and the acid, with the formation of a soluble salt. In those cases where the resultant salt is insoluble, the water still loses its acid reaction, and therefore it may be ascertained, by the addition of an acid, whether a given hydrate has a basic character, like the hydrates of oxide of copper, lead, &c. If the acid does not act on the given insoluble hydrate (at any temperature), then it has not a basic character, and it should be tested as to whether it has an acid character. This is done by taking an alkali, instead of the acid, and by observing whether the unknown hydrate then dissolves, or whether the alkaline reaction (entirely or partially) disappears. Thus it may be proved that hydrate of silica is acid, because it dissolves in alkalis and not in acids. If it be a case of an insoluble intermediate hydrate, then it will be observed to react on both the acid and alkali. An instance of this is hydrate of alumina, which is soluble both in caustic potash and in sulphuric acid.

The **degree of affinity** or chemical **energy** proper to oxides and their hydrates is very variable; some extreme members of the series possess it to a great extent. When acting on each other they evolve a large quantity of heat, and when acting on intermediate hydrates they also evolve heat to a considerable degree, as we saw in the combinations of lime and sulphuric anhydride with water. When extreme oxides combine they form stable salts, which are decomposed with difficulty, and often show characteristic properties. The compounds of the intermediate oxides with each other, or even with basic and acid oxides, present a very different case. However much alumina we may dissolve in sulphuric acid, we cannot saturate the acid properties of the sulphuric acid, and the resulting solution will always have an acid reaction towards litmus. So also, whatever quantity of alumina is dissolved in an alkali, the resulting solution will always present an alkaline reaction.

⁵³ In order to give an idea of the quantity of heat evolved in the formation of salts, I append a table of data for *very dilute aqueous solutions* of acids and alkalis, according to the determinations of Berthelot and Thomsen. The figures are given in major calories—that is, in thousands of units of heat. For example, 49 grams of sulphuric acid, H_2SO_4 , taken in dilute aqueous solution, when mixed with such an amount of a weak solution of caustic soda, NaHO , that a neutral salt is formed (when all the hydrogen of the acid is replaced by the sodium), evolves 15,800 units of heat.

	49 parts of H_2SO_4	63 parts of HNO_3		49 parts of H_2SO_4	63 parts of HNO_3
NaHO . . .	15·8	13·7	MgO . . .	15·6	13·8
KHO . . .	15·7	13·8	FeO . . .	12·5	10·7 (?)
NH_3 . . .	14·5	12·5	ZnO . . .	11·7	9·8
CaO . . .	15·6	13·9	Fe_2O_3 . . .	5·7	5·9
BaO . . .	18·4	13·9			

the chemical character of the oxides and many of the physical properties become hidden in their salts. For example, when gaseous carbonic anhydride combines with a base to form a solid salt, the elasticity of the gas quite disappears in its passage into the salt,⁵⁴ just as the elasticity of hydrogen and oxygen does in the formation of water.

Judging from the above, a salt is a compound of basic and acid oxides, or the result of the action of hydrates of these classes on each other, with separation of water. But salts may be obtained by other methods. It must not be forgotten that basic oxides are formed by metals, and acid oxides usually by non-metals. But metals and non-metals are capable of combining together, and a salt is frequently formed by the oxidation of such a compound. For example, iron very easily combines with sulphur, forming iron sulphide, FeS (as we saw in the Introduction); in air, and especially moist air, this absorbs oxygen, with the formation of the same salt, FeSO_4 , as may be obtained by the combination of the oxides of iron and sulphur ($\text{FeO} + \text{SO}_3$) or of the hydrates of these oxides ($\text{FeH}_2\text{O}_2 + \text{H}_2\text{SO}_4 = \text{FeSO}_4 + 2\text{H}_2\text{O}$). In general, salts are formed in most diverse reactions.^{54a} Hence, it cannot be said or supposed that a salt has the properties of the oxides, or must necessarily contain two kinds of oxides in itself. The derivation of

These figures cannot be considered as the heats of neutralisation, because the water here plays its part. Thus, for instance, sulphuric acid and caustic soda, in dissolving in water, evolve very much heat, and the resultant sodium sulphate, in dissolving in water, very little; consequently, the amount of heat evolved in an anhydrous combination will be different from that evolved in a hydrated combination. Those acids which are not energetic in combining with the quantities of alkalis required for the formation of normal salts of sulphuric or nitric acids always, however, give less heat. For instance, with caustic soda: carbonic acid gives 10.2, hydrocyanic 2.9, and hydrogen sulphide 3.9, major calories. And as feeble bases (for example, Fe_2O_3) also evolve less heat than those which are more powerful, so a certain general correlation between thermochemical data and the degree of affinity shows itself here, as in other cases (see Chapter II., note 7). This does not, however, give any reason for measuring the affinity which binds the elements of salts by the heat of their formation in dilute solutions. This is very clearly demonstrated by the fact that water is able to decompose many salts, and is separated in their formation.

⁵⁴ Carbonic anhydride evolves heat in dissolving in water. The solution easily dissociates and evolves carbonic anhydride, according to the law of Henry and Dalton (see Chapter I.). In dissolving in caustic soda, it either gives a normal salt, Na_2CO_3 , which does not evolve carbonic anhydride, or an acid salt, NaHCO_3 , which easily evolves carbonic anhydride when heated. The same gas, when dissolved in solutions of salts, acts in one or the other manner (see Chapter II., note 38). Here it is seen what a successive series of relations exists between compounds of a different order, between substances of different degrees of stability. By making a distinction between solutions and chemical compounds, we overlook those neutral transitions which in reality exist.

^{54a} For example, the sodium salt of formic acid, CHNaO_2 , is formed by the direct absorption of carbonic acid gas, CO_2 , by sodium hydride, NaH ; ammonium nitrite is formed directly from the nitrogen of the air, N_2 , and water, as a by-product in many cases of oxidation taking place in the air; calcium sulphite is obtained from the oxidation of calcium sulphide and polysulphides, and so on.

salts from oxides is merely one of the methods of their preparation. We saw, for instance, that in sulphuric acid it was possible to replace the hydrogen by zinc, and that by this means zinc sulphate was formed; so likewise the hydrogen in many other acids may be replaced by zinc, iron, potassium, sodium, and a whole series of similar metals, corresponding salts being obtained. The hydrogen of the acid, in all these cases, is exchanged for a metal, and a salt is obtained from the hydrate. Regarding a salt from this point of view, it may be said that **a salt is an acid in which hydrogen is replaced by a metal**. This definition shows that a salt and an acid are essentially compounds of the same series, with the difference that the latter contains hydrogen and the former a metal. Such a definition is more exact than the first definition of salts, inasmuch as it likewise includes those acids which do not contain oxygen, and, as we shall afterwards learn, there is a series of such acids. Such an element as chlorine gives compounds with hydrogen in which the hydrogen may be replaced by a metal, forming substances which in their reactions and external characters resemble the salts formed from oxides. Table salt, NaCl , is an example of this. It may be obtained by the replacement of hydrogen in hydrochloric acid, HCl , by the metal sodium, just as sulphate of sodium, Na_2SO_4 , may be obtained by the replacement of hydrogen in sulphuric acid, H_2SO_4 , by sodium. The external appearance of the resulting products, their neutral reaction, and even their saline taste, show their resemblance to one another.

To the fundamental properties of salts yet another must be added—namely, that they are more or less **decomposed by the action of a galvanic current**. The results of this decomposition are very different according to whether the salt is taken in a fused or dissolved state. But the decomposition may generally be so represented that the metal or cation appears at the electro-negative pole or cathode (like hydrogen in the decomposition of water, or its mixture with sulphuric acid), and the remaining parts of the salt, the anion, appear at the electro-positive pole or anode (where the oxygen of water appears). If, for instance, an electric current acts on an aqueous solution of sodium sulphate, Na_2SO_4 , we may assume that the sodium appears at the negative pole, and oxygen and the anhydride of sulphuric acid, i.e., the anion SO_4 , at the positive pole. But in the solution itself the result is different, for sodium decomposes water with evolution of hydrogen, forming caustic soda; consequently hydrogen will be evolved and caustic soda appear at the negative pole, while at the positive pole the sulphuric anhydride combines with water and forms sulphuric acid, and therefore oxygen

will be evolved and sulphuric acid formed round this pole.⁵⁵ In other cases, when the metal separated is not able to decompose water, it will be deposited in a free state. Thus, for example, in the decomposition of copper sulphate, copper separates out at the cathode, and oxygen and sulphuric acid appear at the anode; and if a copper plate be attached to the positive pole, then the oxygen evolved will oxidise the copper, and the oxide of copper will dissolve and be deposited at the negative pole—that is, a transference of copper from the positive to the negative pole ensues. The galvanoplastic art (electrotyping) is based on this principle.⁵⁶ The most radical and general properties of salts (including also such salts as table salt, which contain no oxygen) may therefore be expressed by representing the salt as composed of a metal M and a haloid X—that is, by expressing the salt by MX. In common table salt the metal is sodium, and the haloid, an elementary body, chlorine. In sodium sulphate, Na_2SO_4 , sodium is again the metal, but the complex group, SO_4 , is the haloid. In sulphate of copper, CuSO_4 , the metal is copper and the haloid the same as in the preceding salt. Such a representation of salts expresses with great simplicity the **capacity of every salt to enter into saline double decompositions with other salts**, this consisting in a mutual replacement of the metals in the salts. This exchange of their metals is the fundamental property of salts.^{56a} In the case of two salts with different metals

⁵⁵ This kind of decomposition may be easily observed by pouring a solution of sodium sulphate into a U-shaped tube and inserting electrodes in the two branches. If the solution be coloured with an infusion of litmus, it will easily be seen that it turns blue at the cathode, owing to the formation of sodium hydroxide, and red at the electro-positive pole, from the formation of sulphuric acid.

⁵⁶ In other cases the decomposition of salts by the electric current may be accompanied by much more complex results. Thus, when the metal of the salt is capable of a higher degree of oxidation, such a higher oxide may be formed at the positive pole by the oxygen which is evolved there. This takes place, for instance, in the decomposition of salts of silver and manganese by the galvanic current, peroxides of these metals being formed. Thus in the electrolysis of a solution of KCl, KClO_4 is formed, while with sulphuric acid (corresponding to SO_3) persulphuric acid, corresponding to S_2O_7 , is formed. But all the phenomena as yet known may be expressed by the above hypothesis, that the current decomposes salts into metals, which appear at the negative pole, and the remaining component parts, which appear at the positive pole. Many physico-chemical researches, starting with those of Faraday, Hittorf, and Kohlrausch, have been made on the mechanism of the transference of the ions, the velocity of their motion and their condition in solutions, especially during the last ten years. Further details on this complex subject and a criticism of the existing theories must be looked for in works on physical chemistry. Here it would be out of place to enlarge upon this subject, all the more so, as it has not yet had any direct influence upon purely chemical knowledge.

^{56a} The presence in salts MX of a metallic element M (in acids it is equivalent to hydrogen, in ammonium salts to ammonium, &c.) capable of easily entering into double decomposition with metals, taken either in the form of other salts, or in general of saline compounds, or else in the form of the metals themselves (especially Na, K, Zn, &c.), forms

and haloids, which are in solution or fused, or in any other manner brought into contact, the metals of these salts will always partially or wholly exchange places. If we designate one salt by MX, and the other by NY, then we either partially or wholly obtain from them new salts, MY and NX. Thus we saw, in the Introduction, that on mixing solutions of table salt, NaCl, and silver nitrate, AgNO₃, a white insoluble precipitate of silver chloride, AgCl, is formed and a new salt, sodium nitrate, NaNO₃, obtained in solution. If the metals of salts exchange places in reactions of double decomposition, it is clear that metals themselves, taken in a separate state, are able to act on salts, as zinc evolves hydrogen from acids, and as iron separates copper from copper sulphate. When, to what extent, and which metals displace each other, and how the metals are distributed between the haloids, will be discussed in Chapter X., where we shall be guided by those reflections and deductions which Berthollet introduced into the science at the beginning of the last century.

According to the above observations, an acid is nothing more than a salt of hydrogen. Water itself may be looked upon as a salt in which the hydrogen is combined with either oxygen or the aqueous radicle, OH; water will then be HOH, and alkalis or basic hydrates, MOH. The group OH, or the **aqueous radicle**, otherwise called **hydroxyl**, may be looked on as a haloid (a special X), like the chlorine in table salt, not only because the element Cl and the group OH very often change places, and combine with one and the same element, but also because free chlorine is very similar in many properties and reactions to peroxide of hydrogen, which has the same composition as the aqueous radicle, as we shall afterwards see in Chapter IV. Alkalis and basic hydrates are also salts consisting of a metal and hydroxyl; for instance,

the fundamental characteristic of the saline substances or primary compound bodies formed by the elements. These primary compounds form the first step in the study of chemistry. The further development of chemistry proved the existence of a vast series of more complex compounds, especially hydrocarbons, which do not evince the clearly expressed peculiarities of salts. Such are chiefly the 'organic' or complex carbon compounds studied by 'organic chemistry.' Although they include their acids, bases, and salts, the primary grouping of the elements of which they are made up is evidently different from that in salts, acids, &c., as the hydrogen in the hydrocarbons from which they proceed has not, or but rarely has (for instance, in acetylene, C₂H₂) the property possessed by 'metallic' hydrogen (as in HCl, H₂SO₄, NaHO, &c.) of being replaced by metals. The cause of this must evidently be looked for in the fundamental properties of the carbon, which enters into the composition of these compounds; but it must be confessed that at present there is no satisfactory or legitimate explanation for these peculiarities (the recognition of 'complex radicles' and such like concessions only presents a scheme or generalisation of the phenomenon, but not an explanation), or of the fundamental difference between the saline compounds of the elements and those organic compounds which do not evince saline properties. This is one of the great problems awaiting solution in chemistry, a science which is, strictly speaking, still young and new.

caustic soda, NaOH , which is therefore termed sodium hydroxide. According to this view, **acid salts** are those in which only a portion of the hydrogen is replaced by a metal, and a portion of the hydrogen of the acid remains. Thus sulphuric acid, H_2SO_4 , not only gives the normal salt Na_2SO_4 , with sodium, but also an acid salt, NaHSO_4 . A **basic salt** is one in which the metal is combined, not only with the haloids of acids, but also with the aqueous radicle of basic hydrates—for example, bismuth gives, not only a normal salt of nitric acid, $\text{Bi}(\text{NO}_3)_3$, but also basic salts, like $\text{Bi}(\text{OH})_2(\text{NO}_3)$.

As basic and acid salts of the oxygen acids contain hydrogen and oxygen, they are able to part with these as water and to give anhydro-salts, which it is evident will be compounds of normal salts with anhydrides of the acids or with bases. Thus the above-mentioned acid sodium sulphate corresponds with the anhydro-salt, $\text{Na}_2\text{S}_2\text{O}_7$, equal to 2NaHSO_4 , less H_2O . The loss of water is here, and frequently in other cases, brought about by heat alone, and therefore such salts are frequently termed **pyro-salts**; for instance, the preceding is sodium pyrosulphate ($\text{Na}_2\text{S}_2\text{O}_7$), or it may be regarded as the normal salt Na_2SO_4 + sulphuric anhydride, SO_3 . **Double salts** are those which contain either two metals, $\text{KAl}(\text{SO}_4)_2$, or two haloids.⁵⁷

⁵⁷ The above-enunciated generalisation of the conception of salts as compounds of the metals (simple, or compound, like ammonium, NH_4), with the haloids (simple, like chlorine, or compound, like cyanogen, CN , or the radicle of sulphuric acid, SO_4), capable of entering into double saline decomposition, which is in accordance with the general data respecting salts, was only gradually arrived at after a succession of most varied *propositions as to the chemical structure of salts*.

Salts belong to the class of substances which have been known since very early times, and have long been investigated in many directions. At first, however, no distinction was made between salts, acids, and bases. Glauber prepared many artificial salts during the latter half of the seventeenth century. Up to that time the majority of salts were obtained from natural sources, and that salt which we have referred to several times—namely, sodium sulphate—was named Glauber's salt, after this chemist. Rouelle distinguished normal, acid, and basic salts, and showed their action on vegetable dyes; but he also confounded many salts with acids (even now every acid salt ought to be regarded as an acid, because it contains hydrogen, which may be replaced by metals, and is hence the hydrogen of an acid). Baumé disputed Rouelle's opinion concerning the subdivision of salts, contending that only normal salts are true salts, and that basic salts are simple mixtures of normal salts with bases, and acid salts, mixtures with acids, since washing alone could remove the base or acid from them. Rouelle, in the middle of the last century, however, rendered a great service to the study of salts and the diffusion of knowledge respecting this class of compounds by his attractive lectures. Like the majority of the chemists of that period, he did not employ the balance in his researches, but satisfied himself with purely qualitative data. The first quantitative researches on salts were carried on about this time by **Wenzel**, who was the director of the Freiberg mines, in Saxony. Wenzel studied the double decomposition of salts, and observed that, in the double decomposition of neutral salts, a neutral salt was always obtained. He proved, by a method of weighing, that this is due to the fact that the saturation of a given quantity of a base requires equal relative quantities of different acids. Having taken two neutral salts—for example, sodium sulphate and calcium nitrate—let us mix their

Inasmuch as oxygen compounds predominate in nature, it should be expected from what has been said above that salts, rather than acids or bases, would occur most frequently in nature, for these latter would

solutions together. Double decomposition takes place, because calcium sulphate is formed, which is almost insoluble. However much we might add of each of the salts, the neutral reaction will still be preserved; consequently the neutral character of the salts is not destroyed by the interchange of metals; that is to say, that quantity of sulphuric acid which saturated the sodium is sufficient for the saturation of the calcium, and that amount of nitric acid which saturated the calcium is enough to saturate the sodium contained in combination with sulphuric acid in sodium sulphate. Wenzel was even convinced that matter does not disappear in nature, and on this principle he corrects, in his *Doctrine of Affinity*, the results of his experiments when he found that he obtained less than he had originally taken. Although Wenzel deduced the law of the double decomposition of salts quite correctly, he did not determine those quantities in which acids and bases act on each other. This was carried out at the end of the eighteenth century by **Richter**. He determined the quantities by weight of the bases which saturate acids, and of the acids which saturate bases, and obtained comparatively accurate results, although his conclusions were not correct, for he states that the quantity of a base saturating a given acid varies in arithmetical progression, and the quantity of an acid saturating a given base in geometrical progression. Richter studied the deposition of metals from their salts by other metals, and observed that the neutral reaction of the solution is not destroyed by this exchange. He also determined the quantities by weight of the metals replacing one another in salts. He showed that copper displaces silver from its salts, and that zinc displaces copper and a whole series of other metals. Those quantities of metals which were capable of replacing one another were termed **equivalents**.

Richter's teaching found no followers, because, although he fully believed in the discoveries of Lavoisier, yet he still held to the phlogistic reasonings which rendered his expositions very obscure. The work of the Swedish savant **Berzelius** in the beginning of the nineteenth century freed the facts discovered by Wenzel and Richter from the obscurity of former conceptions and led to their being explained in accordance with Lavoisier's views, and in the sense of the law of multiple proportions which had already been discovered by Dalton. On applying to salts those conclusions which Berzelius arrived at by a whole series of researches of remarkable accuracy, we arrive at the following law of equivalents—*one part by weight of hydrogen in an acid is replaced by the corresponding equivalent weight of any metal*; and, therefore, when metals replace each other, their respective weights are in the same ratio as their equivalents. Thus, for instance, one part by weight of hydrogen is replaced by 23 parts of sodium, 39 parts of potassium, 12 parts of magnesium, 20 parts of calcium, 28 parts of iron, 108 parts of silver, 33 parts of zinc, &c.; and, therefore, if zinc replaces silver, 33 parts of the zinc will take the place of 108 parts of silver, or 33 parts of zinc will be substituted by 23 parts of sodium, &c.

The doctrine of equivalents would be precise and simple did every metal only give one oxide or one salt. It is rendered complicated from the fact that many metals form several oxides, and consequently offer different equivalents in their different degrees of oxidation. For example, there are oxides containing iron in which its equivalent is 28—this is in the salts formed by the suboxide; and there is another series of salts in which the equivalent of iron equals $18\frac{2}{3}$ —which contain less iron, and consequently more oxygen, and correspond with a higher degree of oxidation—ferric oxide. It is true that the former salts are easily formed by the direct action of metallic iron on acids, and the latter only by a further oxidation of the compound formed already; but this is not always so. In the cases of copper, mercury, and tin, under different circumstances, salts are formed which correspond with different degrees of oxidation of these metals, and many metals have two equivalents in their different salts—that is, in salts corresponding with the

always tend to combine forming salts, especially through the medium of the all-pervading water. And, as a matter of fact, salts are found everywhere in nature. They occur in animals and plants, although in but

different degrees of oxidation. Thus it is impossible to endow every metal with one definite equivalent weight. Hence the conception of equivalents, while playing an important part from an historical point of view, appears, with a fuller study of chemistry, to be but subordinate to a higher conception, with which we shall afterwards become acquainted.

The fate of the theoretical views of chemistry was for a long time bound up with the history of salts. The clearest representation of this subject dates back to Lavoisier, and was systematically developed by Berzelius. This representation is called the **binary theory**. All compounds, and especially salts, are represented as consisting of two parts. Salts are represented as compounds of a basic oxide (a base) and an acid (that is, an anhydride of an acid, then termed an acid), whilst hydrates are represented as compounds of anhydrous oxides with water. Such an expression was employed not only to denote the most usual method of formation of these substances (where it would be quite true), but also to express that internal distribution of the elements by which it was proposed to explain all the properties of these substances. Copper sulphate was supposed to contain two most intimate component parts—copper oxide and sulphuric anhydride. This is an hypothesis. It arose from the so-called **electro-chemical hypothesis**, which supposed the two component parts to be held in mutual union, because one component (the anhydride of the acid) has electro-negative properties, and the other (the base in salts) electro-positive. The two parts are attracted together, like substances having opposite electrical charges. But as the decomposition of salts in a state of fusion by an electric current always gives a metal, that representation of the constitution and decomposition of salts called the **hydrogen theory of acids** is nearer the truth than that which considers salts as made up of a base and an anhydride of an acid. But the hydrogen theory of acids is also a binary hypothesis, and does not contradict the electro-chemical hypothesis, but is rather a modification of it. The binary theory dates from Rouelle and Lavoisier, the electro-chemical aspect was zealously developed by Berzelius, and the hydrogen theory of acids is due to Davy and Liebig.

These hypothetical views simplified and generalised the study of a complicated subject, and served to support further arguments; but when salts were in question it was equally convenient to follow one or the other of these hypotheses. But these theories were brought to bear on all other substances, on all compound substances. Those upholding the binary and electro-chemical hypotheses searched for two anti-polar component parts, and endeavoured to express the process of chemical reactions by electro-chemical and similar differences. As zinc replaces hydrogen, they concluded that it is more electro-positive than hydrogen, whilst they forgot that hydrogen may, under different circumstances, displace zinc—for instance, at a red heat. Chlorine and oxygen were considered as being of opposite polarity to hydrogen, because they easily combine with it; nevertheless both are capable of replacing hydrogen, and, what is very characteristic, in the replacement of hydrogen by chlorine in carbon compounds, not only does the chemical character often remain unaltered, but even the external form may remain unchanged, as was shown by Laurent and Dumas. These considerations undermine the binary, and more especially the electro-chemical, theory. An explanation of known reactions then began to be sought for, not in the difference of the polarity of the different substances, but in the joint influences of all the elements on the properties of the compound formed. This is the reverse of the preceding hypothesis.

This reversal was not, however, limited to the destruction of the tottering foundations of the preceding theory: it proposed a new doctrine, and laid the foundation for the modern progress of our science. This doctrine may be termed the **unitary theory**—that is, it strictly acknowledges the joint influences of the elements in a compound substance, denies the existence of separate and contrary components in them, regards copper

small quantity, because, as forming the last stage of chemical reaction, they are capable of only a few simple chemical transformations. And organisms are bodies in which a series of uninterrupted, varied, and active chemical transformations proceed, whilst salts, which only enter into double decompositions between each other, are little prone to such changes. But organisms always contain salts. Thus, for instance, bones contain calcium phosphate, the juice of grapes potassium tartrate (cream of tartar), certain lichens calcium oxalate, and the shells of mollusca calcium carbonate, &c. As regards water and soil, portions of the earth in which the chemical processes are less active, these are full of salts. Thus the waters of the oceans, and all others (Chap. I.), abound in salts, and in the soil, in the rocks of the earth's crust, in the upheaved lavas, and in the falling meteorites the salts of silicic acid, and especially its double salts, predominate. Saline substances also make up the composition of those limestones which often form mountain chains and whole thicknesses of the earth's strata, these consisting of calcium carbonate, CaCO_3 .

Thus we have seen oxygen in a free state and in various compounds of different degrees of stability, from unstable and slightly stable compounds (like Berthollet's salt and nitre) to the most stable silicon compounds, such as exist in granite. We saw an entirely similar gradation of stability in the compounds of water and of hydrogen. In all its aspects oxygen, as an element, or single substance, remains the same, however varied its chemical states, just as a substance may appear in many different physical states of aggregation. But our notion of the immense variety of the chemical states in which oxygen can occur would not be completely understood if we did not make ourselves acquainted with it in the form in which it occurs in ozone and peroxide

sulphate, for instance, as a strictly definite compound of copper, sulphur, and oxygen; then seeks for compounds which are analogous in their properties, and, placing them side by side, endeavours to express the influence of each element in determining the united properties of its compound. In the majority of cases it arrives at conclusions similar to those which are obtained by the above-mentioned hypotheses, but in certain special cases the conclusions of the unitary theory are in entire opposition to those of the binary theory and its corollaries. Cases of this kind are most often met with in the consideration of compounds of a more complex nature than salts, especially organic compounds containing hydrogen. But it is not in this change from an artificial to a natural system, important as it is, that the chief service and strength of the unitary doctrine lies. By a simple review of the vast store of data regarding the reactions of typical substances, it succeeded from its first appearance in establishing a new and important law; it introduced a new conception into science—namely, the conception of *molecules*, with which we shall soon become acquainted. The deduction of the law and of the conception of molecules has been verified by facts in a number of cases, and was the cause of the majority of chemists of our times deserting the binary theory and accepting the unitary theory, which forms the basis of the present work. **Laurent** and **Gerhardt** must be considered as the founders of this doctrine.

of hydrogen. In these it is most unstable and active, its energy having apparently increased. They illustrate fresh aspects of chemical correlations, and the variety of the forms in which matter can appear stand out clearly. We will therefore consider these two substances somewhat in detail.⁵⁸

⁵⁸ This consignment of ozone and peroxide of hydrogen to a separate chapter is all the more necessary, as the difference between saline oxides (capable of forming acids, bases, and salts) and peroxides, is held to all through this work. The former, which have been cursorily considered in the present chapter, correspond with water, the latter with peroxide of hydrogen and ozone. The peroxides always contain more oxygen than the saline oxides, and easily part with their excess of oxygen, which oxidises and in general reacts like the excess of oxygen in ozone and peroxide of hydrogen. Although in an arithmetical sense peroxide of hydrogen, H_2O_2 , is related to water in the same way as SO_3 to SO_2 , or Cu_2O_2 to Cu_2O or in general a higher degree of oxidation to a lower, yet in its reactions the difference appears to be far deeper, as I trust the reader will gradually recognise. Moreover water and the saline oxides corresponding with it have been studied far more than the peroxides, which play a more modest part in nature and the industries. The peroxides have their own special and important interest, which is not, however, so general a one as that presented by water and salts.

CHAPTER IV

OZONE AND HYDROGEN PEROXIDE—DALTON'S LAW

VAN MARUM, during the eighteenth century, observed that air, when subjected to the action of a series of electric sparks, acquired a peculiar smell and the property of combining with mercury at the ordinary temperature. This was afterwards confirmed by a number of fresh experiments. Even in the simple revolution of an electrical machine, when electricity diffuses into the air or passes through it, the peculiar and characteristic smell of ozone, proceeding from the action of the electricity on the oxygen of the atmosphere, is recognised. In 1840 Professor Schönbein, of Basle, turned his attention to this odoriferous substance, and showed that it is also formed, with the oxygen evolved at the positive pole, in the decomposition of water by the action of a galvanic current; also in the oxidation of phosphorus in damp air, and in the oxidation of a number of other substances (especially turpentine), although it is distinguished for its instability and capacity for oxidising other substances. The same gas is also formed in many cases where oxygen is formed at the ordinary (or a lower) temperature; for instance, in the decomposition of acidulated water by the galvanic current, by the action of gaseous fluorine on water ($3\text{H}_2\text{O} + 3\text{F}_2 = 6\text{HF} + \text{O}_3$), or by the action of sulphuric acid on permanganate of potassium,¹ &c. The characteristic smell of this substance gave it its name, from the Greek ὄζω, 'I emit an odour.' Schönbein pointed out that **ozone** is capable of oxidising many substances on which oxygen does not act at the ordinary temperature. For instance, that it oxidises silver, mercury, charcoal, and iron with great energy at the ordinary

¹ This experiment must be made with small quantities and with caution, as an explosion may easily take place.

Jörissen (1897) found that ozone is formed whenever oxygen oxidises at the ordinary temperature (in the slow oxidation of zinc, of $\text{P}(\text{C}_2\text{H}_5)_3$, of lead in the presence of sulphuric acid, the potassium in KCN in acting on gold, &c.). The molecules of oxygen then, as it were, always split up into two portions, one going to oxidise and the other forming ozone. This coincides with what is said later respecting the difference between oxygen gas, O_2 , and ozone, O_3 , in which only $\frac{1}{3}$ of the oxygen acts.

temperature, decolorises (oxidises) blue indigo and many other organic colouring matters, &c. It might be thought that ozone was some new compound substance, as it was at first supposed to be; but careful observations made in this direction have long since led to the conclusion that ozone is nothing but oxygen altered in its properties. This is most strikingly proved by the complete transformation of oxygen containing ozone into ordinary oxygen when it is passed through a tube heated to 250° . Further, at a low temperature pure oxygen gives ozone when electric sparks are passed through it (Marignac and De la Rive). Hence it is proved, both by synthesis and analysis, that ozone is that same oxygen with which we are already acquainted, only endowed with particular properties and in a particular state. By whatever method it be obtained, the amount of it contained in the oxygen is inconsiderable, generally only a small fraction per cent., rarely 2 per cent., and only under low temperatures as much as 20 per cent. The reason of this must be looked for first in the fact that *ozone in its formation from oxygen absorbs heat*, i.e., evolves heat, in its conversion into ordinary oxygen. If any substance be burnt in a calorimeter at the expense of ozonised oxygen, more heat is evolved than when it is burnt in ordinary oxygen, and Berthelot showed that this difference is very large—namely, 29,600 heat units correspond with every forty-eight parts by weight of ozone. This signifies that the transformation of forty-eight parts of oxygen into ozone is accompanied by the absorption of this quantity of heat, and that the reverse process evolves this quantity of heat. Therefore the passage of ozone into oxygen should take place easily and completely (as an exothermal reaction), like combustion. At 250° ozone entirely disappears, forming oxygen. Any rise of temperature may thus bring about the breaking up of ozone, and as a rise of temperature takes place in the action of an electrical discharge, there are, in an electric discharge, the conditions both for the preparation of ozone and for its destruction. Hence it is clear that the transformation of oxygen into ozone *as a reversible reaction* has a limit when a state of equilibrium is arrived at between the products of the two opposite reactions, that the phenomena of this transformation accord with the phenomena of *dissociation*, and that a fall of temperature should aid the formation of a large quantity of ozone.^{1a} Further, it is evident, from what has been said, that the

^{1a} This conclusion, deduced by me as far back as 1878 (*Moniteur Scientifique*) by conceiving the molecules of ozone (see later) as more complex than those of oxygen, and ozone as containing a greater quantity of heat than oxygen, has been proved experimentally by the researches of Mailfert (1880), who showed that the passage of a silent discharge through a litre of oxygen at 0° may form up to 14 milligrams of ozone, and at -30° up to 60 milligrams; but best of all in the determinations of Chappuis and Haute-

best way of preparing ozone is not by electric sparks,² which raise the temperature, but by the employment of a continual discharge or flow of electricity—that is, by the action of a **silent discharge**.³ For this reason all **ozonisers** (which are of most varied construction), or forms of apparatus for the preparation of ozone from oxygen (or air) by the action of electricity, now usually consist of sheets of metal—for instance, tinfoil—or a solution of sulphuric acid mixed with chromic acid, &c., separated by thin glass surfaces placed at short distances from each other, and between which the oxygen or air to be ozonised is introduced and subjected to the action of the silent discharge.⁴ Thus in Berthelot's

feuille (1880), who found that at a temperature of -25° a silent discharge converted 20 per cent. of oxygen into ozone, whilst at 20° it was impossible to obtain more than 12 per cent., and at 100° less than 2 per cent. of ozone was obtained.

² A series of electric sparks may be obtained by an ordinary electrical machine, the electrophorus machines of Holtz and Teploff, &c., Leyden jars, Ruhmkorff coils, or similar means, when the opposite electricities are able to accumulate at the terminals of conductors, and a discharge of sufficient electrical intensity passes through the non-conducting air or oxygen.

³ A silent discharge is such a combination of opposite statical (potential) electricities as takes place (generally between large surfaces) regularly, without sparks, slowly, and quietly (as in the dispersion of electricity). The discharge is only luminous in the dark; there is no observable rise of temperature, and therefore a larger amount of ozone is formed. But nevertheless, on continuing the passage of a silent discharge through ozone it is destroyed. For the action to proceed well a large surface is necessary, and consequently a source of electricity at a high potential. For this reason the silent discharge is best produced by a Ruhmkorff coil, this being the most convenient means of obtaining statical electricity at a considerable potential when the comparatively feeble current of a galvanic battery is employed.

⁴ *v. Babo's apparatus* was one of the first constructed for ozonising oxygen by means of a silent discharge (and is still one of the best). It is composed of a number (twenty or more) of long, thin, capillary glass tubes closed at one end. A platinum wire, extending along their whole length, is introduced into the other end of each tube, and this end is then fused up round the wire, the end of which protrudes outside the tube. The protruding ends of the wires are arranged alternately on two sides in such a manner that on each side there is an equal number of closed ends and wires. A bunch of such tubes (forty should make a bunch of not more than 1 cm. diameter) is placed in a glass tube, and the ends of the wires are connected with two conductors, and are fused to the ends of the surrounding tube. The discharge of a Ruhmkorff coil is passed through these ends of the wires, and the dry air or oxygen to be ozonised is passed through the tube. If oxygen be passed through, ozone is obtained in large quantities and free from oxides of nitrogen, which are formed to some extent when air is acted on. At low temperatures ozone is formed in large quantities. As ozone acts on corks and indiarubber, the apparatus should be made entirely of glass. With a powerful Ruhmkorff coil and forty tubes the ozonation is so powerful that the gas when passed through a solution of iodide of potassium not only sets the iodine free, but even oxidises it to potassium iodate, so that in five minutes the gas-conducting tube is choked up with crystals of the insoluble iodate. In the majority of ozonisers the two tubes are lined with sheet tin or other metal and oxygen is passed through the annular space through which the silent discharge takes place. This kind of ozoniser may be used for ozonising the air of hospitals, &c., for the purpose of disinfection (Chap. V.). Ozone is employed for bleaching, &c., but its application in general requires perfecting.

apparatus (fig. 41), the glass F and the tube A contain sulphuric acid, connected with the poles of a source of electricity, e.g., with the terminals

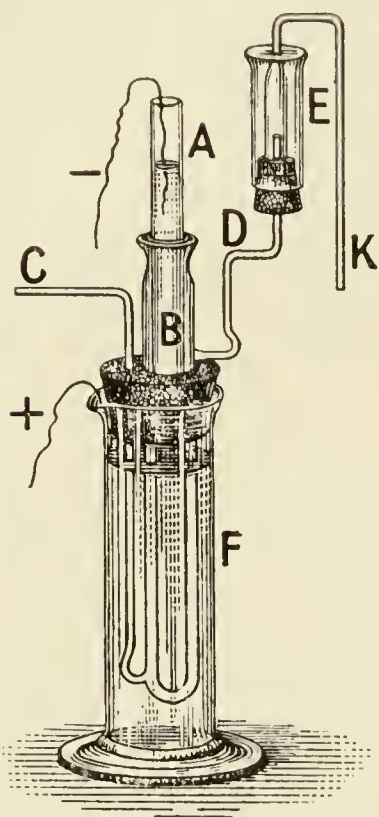


FIG. 41.—Berthelot's apparatus for the production of ozone by the silent discharge.

of a Ruhmkorff's coil. A silent discharge passes through the thin walls of the glass cylinders A and B, over all their surfaces, and consequently, if oxygen be passed through the apparatus by the tube C, it will be ozonised in the annular space between A and B. The ozonised oxygen escapes by the tube D, and may be introduced into any other apparatus.⁵

The properties of ozone⁶ distinguish it in many respects from oxygen. Ozone very rapidly decolorises indigo, litmus, and many other dyes by oxidising them. Silver is oxidised by it at the ordinary temperature, whilst oxygen is not able to oxidise silver even at high temperatures; a bright silver plate rapidly turns black (from oxidation) in ozonised oxygen. It is rapidly absorbed by mercury, forming the oxide; it transforms the lower oxides into

higher—for instance, sulphurous anhydride into sulphuric, nitrous oxide into nitric, arsenious anhydride (As_2O_3) into arsenic anhydride

⁵ In order to connect the ozoniser with any other apparatus it is impossible to make use of indiarubber, mercury, or cements, &c., because they are themselves acted on by, and act on, ozone. All connections must, as was first proposed by Brodie, be hermetically closed by sulphuric acid, which is not acted on by ozone. Thus, a cork is passed over the vertical end of a tube, over which a wide tube passes, so that the end of the first tube protrudes above the cork; mercury is first poured over the cork (to prevent its being acted on by the sulphuric acid), and then sulphuric acid is poured over the mercury. The protruding end of the first tube is covered by the lower end of a third tube immersed in the sulphuric acid.

⁶ The method above described is the only one which has been well investigated. The admixture of nitrogen, or even of hydrogen, and especially of silicon fluoride, appears to aid the formation and preservation of ozone. Amongst other methods for preparing ozone we may mention the following:—1. In the action of oxygen on phosphorus at the ordinary temperature, a portion of the oxygen is converted into ozone. At the ordinary temperature a stick of phosphorus, partially immersed in water and partially in air in a large glass vessel, causes the air to acquire the odour of ozone. It must further be remarked that if the air be left for long in contact with the phosphorus, or without the presence of water, the ozone formed is destroyed by the phosphorus. 2. By the action of sulphuric acid on peroxide of barium. If the latter be covered with strong sulphuric acid (the acid, if diluted with only one-tenth of water, does not give ozone), then at a low temperature the oxygen evolved contains ozone, and in much greater quantities than is obtained by the action of electric sparks or phosphorus. 3. Ozone may also be obtained by decomposing strong sulphuric acid by potassium manganate, especially with the addition of barium peroxide.

(As_2O_5), &c.⁷ But what is especially characteristic in ozone is the decomposing action it exerts on potassium iodide. Oxygen does not act on this salt, but ozone passed into a solution of potassium iodide **liberates iodine**, whilst the potassium is obtained as caustic potash, which remains in solution: $2\text{KI} + \text{H}_2\text{O} + \text{O} = 2\text{KHO} + \text{I}_2$. As the presence of minute traces of free iodine may be discovered by means of starch, with which it forms a very dark blue-coloured substance, a mixture of potassium iodide with starch paste will detect the presence of very small traces of ozone.⁸ Ozone is destroyed or converted into ordinary oxygen not only by heat, but also by long keeping, especially in the presence of alkalis, peroxide of manganese, chlorine, &c., and also when it acts by oxidation (see later).

⁷ It is said that ozone oxidises water and converts it into peroxide of hydrogen. Ozone takes up the hydrogen from hydrochloric acid; chlorine is liberated, and can dissolve gold. Iodine is directly oxidised by ozone, but not by oxygen. Ammonia, NH_3 , is oxidised by ozone into ammonium nitrite (and nitrate), $2\text{NH}_3 + \text{O} = \text{NH}_4\text{NO}_2 + \text{H}_2\text{O}$, and therefore a drop of ammonia, on falling into the gas, gives a thick cloud of the salts formed. Ozone converts colourless lead oxide into brown dioxide, and suboxide of thallium (which is colourless) into oxide (which is brown), so that this reaction is made use of for detecting the presence of ozone. Lead sulphide, PbS (black), is converted into sulphate, PbSO_4 (colourless), by ozone. A neutral solution of manganese sulphate gives a precipitate of manganese peroxide, and an acid solution may be oxidised into permanganic acid, HMnO_4 . With respect to the oxidising action of ozone on organic substances, it may be mentioned that with ether, $\text{C}_4\text{H}_{10}\text{O}$, ozone gives ethyl peroxide, which is capable of decomposing with explosion (according to Berthelot), and is decomposed by water into alcohol, $2\text{C}_2\text{H}_5\text{O}$, and hydrogen peroxide, H_2O_2 .

⁸ This reaction is the one usually made use of for detecting the presence of ozone. In the majority of cases paper is soaked in solutions of potassium iodide and starch. Such **ozonometrical** or iodised starch-paper, when damp, turns blue in the presence of ozone, and the tint obtained varies considerably (to black), according to the length of time it is exposed and to the amount of ozone present. Even the amount of ozone in a given gas may to a certain degree be judged by the shade of colour acquired by the paper if preliminary tests be made.

Test-paper for ozone is prepared in the following manner:—One gram of neutral potassium iodide is dissolved in 100 grams of distilled water; 10 grams of starch are then shaken up in the solution, and the mixture is boiled until the starch is converted into a jelly. This jelly is then smeared over blotting-paper and left to dry. It must be remarked, however, that *the colour of iodised starch-paper is changed, not only by the action of ozone, but by that of many other oxidisers*, the oxides of nitrogen (especially N_2O_4) and hydrogen peroxide. Houzeau proposed soaking common litmus-paper with a solution of potassium iodide, which in the presence of ozone would turn blue, owing to the formation of KHO. In order to determine if the blue colour is not produced by an alkali (ammonia) in the gas, a portion of the paper is not soaked in the potassium iodide, but moistened with water: this portion will then also turn blue if ammonia be present. A reagent for distinguishing ozone from hydrogen peroxide with certainty is not known, and therefore these substances in very small quantities (for instance, in the atmosphere) may easily be confounded. Formerly the mistake has frequently been made of ascribing the alteration of iodised starch-paper in the air to the presence of ozone (note 13a); at the present time there is reason to believe that it is most often due to the presence of nitrous acid (Illosvay, 1889).

Hence **ozone**, although it has the same **composition as oxygen**, differs from it in stability, and by the fact that it **oxidises** a number of substances very **energetically** at the ordinary temperature. In this respect ozone resembles the oxygen of certain unstable compounds, or oxygen at the moment of its liberation.

In ordinary oxygen and ozone we see an example of one and the same substance, in this case an element, appearing in two states. This indicates that the properties of a substance, and even of an element, may vary without its composition varying. Very many such cases are known. Such cases of a chemical transformation which determines a difference in the properties of one and the same element are termed cases of **isomerism**. The isomerism of elements is termed **allotropy**. The cause of isomerism evidently lies deep within the essential nature of a substance, and its investigation has already led to a number of results of unexpected importance and of immense scientific significance. It is easy to understand the difference between substances containing different elements or the same elements in different proportions. That a difference should exist in these cases necessarily follows, if, as our knowledge compels us, we admit that there is a radical difference between the various simple bodies or elements. But when the composition—i.e., the quality and quantity—of the elements in two substances is the same and yet their properties are different, it is clear that the conceptions of diverse elements and of the varying composition of compounds alone are insufficient for the expression of all the diversity of properties of matter in nature. Something else, still more profound and internal than the composition by weight of substances, must, judging from isomerism, determine the properties and transformation of substances.^{8a}

^{8a} Under that atomic (Chap. VII.) conception of matter which is recognised by modern science, isomerism cannot be regarded otherwise than as a modification in the distribution of similar atoms in space, that is, with respect to each other. Hence, among isomerides, we distinguish polymerides, which differ from each other chiefly in the number of atoms forming the individual system or molecule of the substance. Thus ozone, O_3 , by its density, is regarded as the polymeride of oxygen, O_2 . But isomerism may also occur with an equal number of atoms in the molecules, if their mutual distribution or *structure* (constitution) be different. In organic chemistry, where polymerides and other isomerides are very frequent, it is especially important to have in view not only the composition but also the structure of compounds. But this is a matter of secondary importance in the study of the elements, which forms the main object of the present work, because the properties of substances are chiefly determined by the properties of the elements they contain, and the main problem of study should be deducing the properties of substances from those of the elements, and therefore I consider the chief object of this work to be an expression of the properties of the chemical elements. And as the chemical elements can only be conceived from the simple and compound substances they form, they compose the chief subject of our work. It does not aim at embracing the whole province of

On what are the isomerism of ozone and oxygen, and the peculiarities of ozone, dependent? On what, besides the extra store of energy, which clearly expresses the peculiarities of ozone, rests the cause of its difference from oxygen? These questions for long occupied the minds of investigators, and were the motive for the most varied, exact, and accurate researches, which were chiefly directed to the study of the volumetric relations exhibited by ozone. In order to acquaint the reader with the previous researches of this kind, I cite the following from a memoir by Soret, in the 'Transactions of the French Academy of Sciences' for 1866:

'Our present knowledge of the volumetric relations of ozone may be expressed in the following manner:

'1. "Ordinary oxygen in changing into ozone under the action of electricity shows a diminution in volume." This was discovered by Andrews and Tait.

'2. "In acting on ozonised oxygen with potassium iodide and other substances capable of being oxidised, we destroy the ozone, but the volume of the gas remains unchanged." For the researches of Andrews, Soret, von Babo, and others showed that the proportion of ozonised oxygen absorbed by the potassium iodide is equal to the original contraction of volume of the oxygen—that is, in the absorption of the ozone the volume of the gas remains unchanged. From this it might be imagined that ozone, so to speak, occupies no space—is indefinitely dense.

'3. "By the action of heat ozonised oxygen increases in volume, and is transformed into ordinary oxygen. This increase in volume corresponds with the quantity of ozonised oxygen which is given up to the potassium iodide in its decomposition" (the same observers).

'4. These unquestionable experimental results lead to the conclusion that ozone is denser than oxygen, and that in its oxidising action it gives off that portion of its substance to which is due the increased density distinguishing it from ordinary oxygen.'

If we imagine (says Weltzien) that n volumes of ozone consist of n volumes of oxygen combined with m volumes of the same substance, and that ozone in oxidising gives up m volumes of oxygen and leaves n volumes of ordinary oxygen gas, then all the above facts can be explained; otherwise it must be supposed that ozone is infinitely dense. 'In order to determine the density of ozone' (we again cite Soret) 'recourse cannot be had to the direct determination of the weight of a given

chemistry, but only at acquainting the reader with that portion which concerns the doctrine of the chemical elements. In this respect it forms an introduction to chemistry as a science, but even then it is impossible to avoid mentioning the fundamental conceptions of structure and isomerism.

volume of the gas, because ozone cannot be obtained in a pure state. It is always mixed with a very large quantity of oxygen. It was necessary, therefore, to have recourse to such substances as would absorb ozone without absorbing oxygen and without destroying the ozone. Then the density might be deduced from the decrease of volume produced in the gas by the action of such solvents in comparison with the quantity of oxygen given up to potassium iodide. Advantage must also be taken of the determination of the increase of volume produced by the action of heat on ozone, if the volume occupied by the ozone before heating be known.' Soret found two such substances, turpentine and oil of cinnamon. 'Ozone disappears in the presence of turpentine. This is accompanied by the appearance of a dense vapour, which fills a vessel of small capacity (0.14 litre) to such an extent that it is impenetrable to direct solar rays.' On measuring the gaseous volume before and after the action of both volatile oils, a considerable decrease is remarked. On applying all the necessary corrections (for the solubility of oxygen in the oily liquids named above, for the pressures of their vapour, for the change of pressure, &c.) and making a series of comparative determinations, Soret obtained the following result: two volumes of ozone capable of being dissolved, when changed to ordinary oxygen (by heating with a wire brought to a red heat by a galvanic current) increase by one volume. Hence it is evident that in the formation of ozone three volumes of oxygen give two volumes of ozone—that is, its density (referred to hydrogen) is 24 if the density of oxygen is 16. Ladenburg (1900) verified and confirmed Soret's conclusion by a modified method and direct weighings.

The observations and determinations of Soret showed, therefore, that ozone is heavier than oxygen, and even than carbonic anhydride (because ozonised oxygen passes through fine orifices more slowly than either pure oxygen or its mixtures with carbonic anhydride), although lighter than chlorine (it flows more rapidly through such orifices than chlorine), and they indicated that **ozone is one and a half times denser than oxygen**, which may be expressed by designating a molecule of oxygen by O_2 and of ozone by O_3 , and hence ozone, OO_2 , is comparable with compound substances⁹ formed by oxygen, as, for instance, CO_2 ,

⁹ Ozone is, as it were, an oxide of oxygen, just as water is an oxide of hydrogen. Just as aqueous vapour is composed of two volumes of hydrogen and one volume of oxygen, which on combining condense into two volumes of aqueous vapour, so also two volumes of oxygen are combined with one volume of oxygen to give two volumes of ozone. In the action of ozone on different substances it is only that additional portion of the molecule, by which it differs from ordinary oxygen, that combines with other bodies, and that is why, under these circumstances, the volume of the ozonised oxygen does not change. Starting with two volumes of ozone, one-third of its weight is parted with, and two volumes of oxygen remain.

SO₂, NO₂, &c. This explains the chief differences between ozone and oxygen, and the cause of the isomerism, and at the same time leads one to expect ¹⁰ that ozone, being a gas which is denser than oxygen, would be liquefied much more easily. This was actually shown to be the case by Chappuis and Hautefeuille in 1880, in their researches on the **physical properties of ozone**, and therefore if ozonised air or oxygen be passed through a tube cooled by liquid air, the ozone is converted into a blue liquid of sp. gr. 1.46, which must be manipulated with extreme caution, as it passes into ordinary oxygen at the ordinary temperature, with the evolution of heat and violent explosion (owing to the rapid increase in volume). Its boiling-point under a pressure of 760 mm. is about -106° according to Olzewsky, and -125° according to Ladenburg. Liquid and compressed ¹¹ ozone is **sky-blue**. It explodes violently when suddenly compressed and heated, changing into ordinary oxygen and evolving, like all explosive substances, ¹² that excess of heat which distinguishes it from oxygen.

Thus, judging by what has been said above, ozone should be formed in nature, not only in the many processes of oxidation which go on, but also by the condensation of atmospheric oxygen. The significance of

The above observations of Soret on the capacity of turpentine for dissolving ozone, together with Schönbein's researches on the formation of ozone in the oxidation of turpentine and of similar volatile vegetable oils (entering into the composition of *perfumes*), also explain the action of this ethereal oil on a great many substances. It is known that turpentine oil, when mixed with many substances, promotes their oxidation. In this case it probably not only itself promotes the formation of ozone, but also dissolves ozone from the atmosphere, and thus acquires the property of oxidising many substances. It bleaches linen and cork, decolorises indigo, promotes the oxidation and hardening of boiled linseed oil, &c. These properties of turpentine oil are made use of in practice. Dirty linen and many stained materials are easily cleaned by turpentine, not only because it dissolves the grease, but also because it oxidises it. The admixture of turpentine with drying (boiled) oil, oil-colours, and lacs aids their rapid drying because it attracts ozone. Ozonisation perhaps explains the refreshing influence ethereal oils have in scents and other similar preparations, and also the salubrity of the air of pine forests. Water upon which a layer of turpentine oil has been poured acquires, when left standing in the light, the disinfecting and oxidising properties of ozonised turpentine (is this due to the formation of H₂O₂?).

¹⁰ The densest, most complex, and heaviest particles of matter, under similar conditions, should evidently be less capable of passing into a state of gaseous motion, should sooner attain a liquid state, and have a greater cohesive force. These theoretical premises, having been verified, do much to confirm the modern (Avogadro-Gerhardt's) theory of chemical molecules.

¹¹ The blue colour proper to ozone may be seen through a tube one metre long, filled with oxygen, containing 10 per cent. of ozone.

¹² All explosive bodies and mixtures (gunpowder, detonating gas, &c.) evolve heat in exploding—that is, the reactions which accompany explosions are exothermal. In this manner ozone in decomposing evolves latent heat, although generally heat is absorbed in decomposition. This shows the meaning and cause of explosion.

ozone in nature has often arrested the attention of observers. There is a series of ozonometrical observations which show the different amounts of ozone in the air at different localities, at different times of the year, and under different circumstances. But the observations made in this direction cannot be considered as sufficiently exact, because the methods in use for determining ozone were not quite accurate. It is, however, indisputable¹³ that the amount of ozone in the atmosphere is subject to variation; that the air of dwellings contains no ozone (it disappears in oxidising organic matter); that the air of fields and forests always contains ozone, or substances (peroxide of hydrogen) which act like it (on iodised starch paper, &c.)^{13a}, that the amount of ozone increases after storms; and that miasmata, &c., are destroyed by ozonising the atmosphere. It readily oxidises organic substances, and miasmata are produced by organic substances and the germs of organisms, all of which are easily changed and oxidised. Indeed, many miasmata—for instance, the volatile substance of decomposing organisms—are clearly destroyed or changed, not only by ozone, but also by many other powerfully oxidising substances, such as peroxide of hydrogen, chlorine water, potassium permanganate, and the like.¹⁴ All that is now known respecting the presence of ozone in the air may be summed up in the following words: A small quantity of an oxidising substance, resembling ozone in its reactions, has undoubtedly been observed and determined in the atmosphere, especially in fresh air, for instance after a storm; and it is very likely that this substance contains a mixture of such oxidising substances as ozone, peroxide of hydrogen, and the lower oxides of nitrogen (especially nitrous acid and its ammonium salt)

¹³ In Paris it has been found that the further one goes from the centre of the town the greater becomes the amount of ozone in the air. The reason of this is evident: in a city there are many conditions for the destruction of ozone. This is why we distinguish country air from that of cities by its freshness. In spring the air contains more ozone than in autumn; the air of fields more than the air of towns.

^{13a} The question of the presence of ozone in the air has not yet been fully elucidated, as those reactions by which ozone is generally detected are also common to nitrous acid (and its ammonium salt). Ilosvay de Ilosva (1889), in order to exclude the influence of such bodies, passed air through a 40 per cent. solution of caustic soda, and then through a 20 per cent. solution of sulphuric acid (these solutions, according to this author, do not destroy ozone), and tested the air thus purified for the presence of ozone. As no ozone was then detected, the author concludes that all the effects which were formerly ascribed to ozone should be referred to nitrous acid. But this conclusion requires more careful verification since the researches of Professor Schönbein on the presence of peroxide of hydrogen in the atmosphere.

¹⁴ The oxidising action of ozone may be taken advantage of for technical purposes; for instance, for destroying colouring matters. It has even been employed for bleaching tissues and for the rapid preparation of vinegar, although these methods have not yet received wide application.

produced from the elements of the atmosphere by oxidation and by the action of electrical discharges.¹⁵

Thus in ozone we see (1) the capacity of elements (and it must be all the more marked in compounds) of changing in properties without altering in composition; this is termed **isomerism**; (2) the capacity of certain elements for condensing themselves into molecules of different densities; this forms a special case of isomerism called **polymerism**; (3) the capacity of oxygen for appearing in a still more active and energetic chemical state than that in which it occurs in ordinary gaseous oxygen; and (4) the formation of unstable equilibria or chemical states, which are illustrated both by the ease with which ozone acts as an oxidiser and by its capacity for decomposing with explosion.¹⁶

Hydrogen peroxide.—Many of those properties which we have seen in ozone belong also to a peculiar substance containing oxygen and hydrogen and called hydrogen peroxide or oxygenated water. This substance was discovered in 1818 by Thénard. When heated it is decomposed into water and oxygen, evolving as much oxygen as is contained in the water remaining after the decomposition. That portion of oxygen by which hydrogen peroxide differs from water behaves in a number of cases just like the active oxygen in ozone, which distinguishes it from ordinary oxygen. In H_2O_2 , and in O_3 , one atom of oxygen acts as a powerful oxidiser, and on separating out it leaves H_2O or O_2 , which do not act so energetically, although they still contain oxygen.¹⁷ Both H_2O_2 and O_3 contain the oxygen, as it were, in a condensed state, and when freed from pressure by the forces (internal) of the elements in another substance, this oxygen is easily evolved, and therefore acts as oxygen does at the moment of its liberation. Both substances in decomposing, with the separation of a portion of their oxygen, *evolve* heat, whilst decomposition is usually accompanied by an absorption of heat.

¹⁵ The connection between ozone and peroxide of hydrogen, presently to be described, is so great that wherever one of them occurs, the other is sure to be found if the reaction proceeds in the presence of water; for instance, in the preparation of ozone by phosphorus, in flames, or by the action of BaO_2 on H_2SO_4 , &c. But this is readily understood if ozone and water form peroxide of hydrogen, as is now supposed. This reaction is probably expressed by the equation, $\text{O}_3 + \text{H}_2\text{O} = \text{O}_2 + \text{H}_2\text{O}_2$, although experimental proofs are yet wanting to confirm this.

¹⁶ A number of substances resemble ozone in one or other of these respects. Thus cyanogen, C_2N_2 , nitrogen chloride, &c., decompose with explosion and evolution of heat. Nitrous anhydride, N_2O , forms a blue liquid like ozone, and in a number of cases oxidises like ozone.

¹⁷ It is evident that there is a want of words here for distinguishing oxygen, O , as an ultimate **element** from oxygen, O_2 , as a **free element**. The latter should be termed oxygen gas did not custom and the length of the expression render it inconvenient.

Hydrogen peroxide is formed under many circumstances by combustion and oxidation, but in very limited quantities; thus, for instance, it is sufficient to shake up zinc with sulphuric acid, or even with water, to observe the formation of a certain quantity of hydrogen peroxide in the water.¹⁸ From this cause, probably, a series of different oxidation processes are accomplished in nature, and according to Professor Schöne, of Moscow, hydrogen peroxide occurs in the atmosphere, although in variable and small quantities, and probably its formation is connected with ozone, with which it has much in common. There is reason to think (but it has not been proved) that peroxide of hydrogen is directly formed by the action of ozone on water. The usual mode of formation of hydrogen peroxide, and the method by which it may be indirectly obtained,¹⁹ is by the double decomposition of an acid and

¹⁸ Schönbein states that the formation of hydrogen peroxide is to be remarked in every oxidation in water or in the presence of aqueous vapour. According to Struve, hydrogen peroxide is contained in snow and in rain water, and its formation, together with that of ozone and ammonium nitrate, is even probable in the processes of respiration and combustion. A solution of tin in mercury, or liquid tin amalgam, when shaken up in water containing sulphuric acid, produces hydrogen peroxide, whilst iron under the same circumstances does not give rise to its formation. The presence of small quantities of hydrogen peroxide in these and similar cases is recognised by many reactions. Among them, the action **on chromic acid** in the presence of ether is very characteristic. Hydrogen peroxide converts the chromic acid into a higher oxide, Cr_2O_7 , which is of a dark-blue colour and dissolves in ether. This ethereal solution is to a certain extent stable, and therefore the presence of hydrogen peroxide may be recognised by mixing the liquid to be tested with ether and adding a few drops of a solution of chromic acid. On shaking the mixture, the ether dissolves the higher oxide of chromium which is formed, and on rising to the top acquires a blue colour. The formation of hydrogen peroxide in the combustion and oxidation of substances containing or evolving hydrogen must be understood in the light of the conception, to be considered later, of molecules occupying equal volumes in a gaseous state. At the moment of its evolution a molecule H_2 combines with a molecule O_2 , and gives H_2O_2 . As this substance is unstable, a large proportion of it is decomposed, a small amount only remaining unchanged. If it is obtained, water is easily formed from it: this reaction evolves heat, and the reverse action is not very probable. Direct determinations show that the reaction, $\text{H}_2\text{O}_2 = \text{H}_2\text{O} + \text{O}$, evolves 22,000 heat units. From this it will be understood how easy is the decomposition of hydrogen peroxide, as well as the fact that a number of substances which are not directly oxidised by oxygen are oxidised by hydrogen peroxide or by ozone, which also evolves heat on decomposition. Such a representation of the origin of hydrogen peroxide was developed by me about 1870. Subsequently (1890) Traube has pronounced a similar opinion, stating that Zn under the action of water and air gives, besides ZnH_2O_2 , also H_2O_2 .

¹⁹ The formation of hydrogen peroxide from barium peroxide by a method of double decomposition is an instance of a number of **indirect methods of preparation**. A substance A does not combine with B, but A B is obtained from A C in its action on B D (see Introduction) when C D is formed. Water does not combine with oxygen, but when present in an acid it acts on the compound of oxygen with barium oxide, because this oxide gives a salt with an acid anhydride. It is to be remarked that the passage of barium oxide, BaO , into the peroxide, BaO_2 , is accompanied by the **evolution** of 12,100 heat units per 16 parts of oxygen by weight combined, but the passage of H_2O into the peroxide H_2O_2 does not proceed directly, because it would be accompanied by the **absorp-**

the peroxides of certain metals, especially those of potassium, calcium, and barium.²⁰ We saw, when speaking of oxygen (Chap. III.), that it is only necessary to heat the anhydrous oxide of barium to a red heat in a current of air or oxygen (or, better still, to heat it with potassium chlorate, and then to wash away the potassium chloride formed) to obtain peroxide of barium.²¹ Barium peroxide gives hydrogen peroxide by the action of dilute acids in the cold.²² The process of decomposition is very clear in this case: the hydrogen of the acid replaces the barium of the peroxide, a barium salt of the acid being formed, while the hydrogen peroxide formed in the reaction remains in solution.²³

tion of 22,000 units of heat per 16 parts by weight of oxygen combined. Barium peroxide, in acting on an acid, evidently evolves less heat than the oxide, and it is this difference of heat that is absorbed in the hydrogen peroxide.

²⁰ Dioxides of lead and manganese, and other analogous peroxides (see Chap. III., note 9), do not give hydrogen peroxide under these conditions, but yield chlorine with hydrochloric acid.

²¹ The impure barium peroxide obtained in this manner may be easily purified. For this purpose it is dissolved in a dilute solution of nitric acid. A certain quantity of an insoluble residue always remains, from which the solution is separated by filtration. The solution will contain not only the compound of the barium peroxide, but also a compound of the barium oxide itself, a certain quantity of which always remains uncombined with oxygen. The acid compounds of the peroxide and oxide of barium are easily distinguishable by their different stability. The peroxide gives an unstable compound, and the oxide a stable salt. By adding an aqueous solution of barium oxide to the resultant solution, the whole of the peroxide contained in the solution may be precipitated as a pure aqueous compound (Kouriloff, 1889, obtained the same result by adding an excess of BaO_2). The first portions of the precipitate will consist of impurities—for instance, oxide of iron—which are rejected. The barium peroxide then separates out, and is collected on a filter and washed; it forms a substance having a definite composition, $\text{BaO}_2 \cdot 8\text{H}_2\text{O}$. Pure hydrogen peroxide should always be prepared from such purified barium peroxide.

²² In the cold, strong sulphuric acid with barium peroxide gives ozone; when diluted with a certain amount of water it gives oxygen (see note 6), whilst hydrogen peroxide is only obtained by the action of very weak sulphuric acid. Hydrochloric, hydrofluoric, carbonic, hydrofluosilicic, and other acids, when diluted with water, also give hydrogen peroxide with barium peroxide. Schöne, who very carefully investigated hydrogen peroxide, showed that it is formed by the action of many of the above-mentioned acids on barium peroxide. In preparing peroxide of hydrogen by means of sulphuric acid, the solution must be kept cold. A solution of maximum concentration may be obtained by successive treatments with sulphuric acid of increasing strength. In this manner a solution containing from 2 to 3 grams of pure peroxide in 100 c.c. of water may be obtained.

²³ With the majority of acids, the salt of barium which is formed remains in solution; thus, for instance, by employing hydrochloric acid, hydrogen peroxide and barium chloride remain in solution. Complicated processes would be required to obtain pure hydrogen peroxide from such a solution. It is much more convenient to take advantage of the action of carbonic anhydride on the pure hydrate of barium peroxide (note 21). For this purpose the hydrate is stirred up in water, and a rapid stream of carbonic anhydride is passed through the water. Barium carbonate, insoluble in water, is formed, and the hydrogen peroxide remains in solution, so that it may be separated from the carbonate by filtering. Sometimes hydrofluosilicic acid is employed, its barium salt being also insoluble in water. The purest H_2O_2 is obtained by distilling *in vacuo*. But in the absence of water it easily decomposes, and cannot be kept for long. It keeps better if a small amount of acid be added to it.

The reaction is expressed by the equation, $\text{BaO}_2 + \text{H}_2\text{SO}_4 = \text{H}_2\text{O}_2 + \text{BaSO}_4$. It is best to take a cold dilute solution of sulphuric acid and to almost saturate (testing with litmus) it with barium peroxide, so that a small excess of acid remains; insoluble barium sulphate is formed. A more or less dilute (3–4 per cent.) aqueous solution of hydrogen peroxide is obtained. This solution may be concentrated, that is to say, evaporated in a vacuum over sulphuric acid. In this way the water may even be entirely evaporated from the solution of the hydrogen peroxide; but in this case it is necessary to work at a low temperature, and not keep the peroxide long in the rarefied atmosphere, as otherwise it decomposes.^{23a} A solution of peroxide of hydrogen (mixed with the solution of a salt of sodium, NaX) is used for bleaching (especially silk and wool) on a large scale, and is now usually prepared from peroxide of sodium, Na_2O_2 , by the action of dilute acids: $\text{Na}_2\text{O}_2 + 2\text{HX} = 2\text{NaX} + \text{H}_2\text{O}_2$.²⁴

When pure, hydrogen peroxide is a colourless liquid, without smell, and having a very unpleasant taste—such as belongs to the salts of many metals—the so-called ‘metallic’ taste. Water stored in zinc vessels has this taste, which is probably due to its containing hydrogen peroxide. The pressure of the vapour of hydrogen peroxide is less than that of aqueous vapour; this enables its solutions to be concentrated in a vacuum. The specific gravity of anhydrous hydrogen peroxide is 1.455–1.5. It has a bluish tint and decomposes, with the evolution of oxygen, when heated, especially if it is not perfectly pure. But if no solid powdery matter be present it evaporates without decomposition when heated under a low pressure (10–50 mm. of mercury). This is taken advantage of to obtain it pure. The water then passes over first, because it boils at a lower temperature. The more dilute the aqueous solution, the more stable it is. Very weak solutions may be distilled without decomposing the hydrogen peroxide. It decolorises solutions of litmus and turmeric, and acts in a similar oxidising manner on many colouring matters of organic origin (for which reason it is employed for bleaching tissues).^{24a}

^{23a} Hydrogen peroxide may be extracted from very dilute solutions by means of ether, which dissolves it. A solution of hydrogen peroxide in water may be concentrated by cooling it to a low temperature, when the water crystallises out—that is, is converted into ice—whilst the hydrogen peroxide remains in solution, as it only freezes at very low temperatures (in liquid air). It must be observed that hydrogen peroxide, in a strong solution in a pure state, is exceedingly unstable even at the ordinary temperature, and it must therefore be preserved in vessels always kept cold, as otherwise it evolves oxygen and forms water.

²⁴ Peroxide of sodium (Chap. XII., note 49) is prepared by burning sodium in dry air.

^{24a} Peroxide of hydrogen has an industrial application in the arts; for instance, (1) as a bleaching agent, it having the important advantage over chloride of lime, SO_2 , &c., of

Many substances decompose hydrogen peroxide, forming water and oxygen, without apparently suffering any change. In this case, substances in a state of fine division show a much quicker action than compact masses, from which it is evident that the action is here based on contact (see Introduction). It is sufficient to bring hydrogen peroxide into contact with charcoal, gold, dioxide of manganese, the alkalis, metallic silver, or platinum, to bring about the above decomposition,²⁵ which, if proceeding very rapidly with pure peroxide or strong solutions, may lead to an explosion. Besides which, hydrogen peroxide forms water and parts with its oxygen with great ease to a number of substances which are capable of being oxidised or of combining with oxygen, and in this respect is very like ozone and other **powerful oxidisers**.²⁶ To the class of contact phenomena, which

not acting upon the material under treatment: it may be used for bleaching feathers, hair, silk, wool, wood, &c., and it also removes stains of all kinds, such as wine, ink, and fruit-stains; (2) it destroys bacteria, as does ozone, without having any injurious effect upon the human body. It can also be used for washing all kinds of wounds, for purifying the air in the sick-room, &c.; and (3) as a preserving agent for potted meats, &c. A small amount of sulphuric acid is often added to the aqueous (3 per cent.) solution in order to store it for industrial purposes.

²⁵ As the result of careful research, certain of the *catalytic* or contact phenomena have been subjected to exact explanation, which shows that some substance present participates in these reactions, but does not affect the series of changes proceeding from mechanical actions alone. Thus, for instance, Schöne showed that with hydrogen peroxide, alkalies give peroxides of the alkaline metals, which combine with the remaining hydrogen peroxide, forming unstable compounds which are easily decomposed, and therefore alkalies evince a decomposing (catalytic) influence on solutions of hydrogen peroxide. Only acid solutions of hydrogen peroxide, and then only dilute ones, can be preserved well.

²⁶ **Hydrogen peroxide**, as a substance containing much oxygen (namely, 16 parts to one part by weight of hydrogen), exhibits many **oxidising reactions**. Thus, it oxidises arsenic, converts lime into calcium peroxide and the oxides of zinc and copper into peroxides. It parts with its oxygen to many sulphides, converting them into sulphates, &c.; thus, it converts black lead sulphide, PbS , into white lead sulphate, PbSO_4 , copper sulphide into copper sulphate, and so on. The restoration of old oil paintings by hydrogen peroxide is based on this action. Oil colours are usually admixed with white lead, and in many cases the colour of oil-paints becomes darker in process of time. This is partly due to the sulphuretted hydrogen contained in the air, which acts on white lead, forming lead sulphide, which is black. The intermixture of the black colour darkens the rest. In cleaning a picture with a solution of hydrogen peroxide, the black lead sulphide is converted into white sulphate, and the colours brighten owing to the disappearance of the black substance which previously darkened them. Hydrogen peroxide oxidises with particular energy substances containing hydrogen and capable of easily parting with it to oxidising substances. Thus it decomposes hydriodic acid, setting the iodine free and converting the hydrogen it contains into water; it also decomposes sulphuretted hydrogen in exactly the same manner, setting the sulphur free. Starch paste with potassium iodide is not, however, directly coloured by peroxide of hydrogen in the entire absence of free acids; but the addition of a small quantity of ferrous sulphate (green vitriol) or of lead acetate to the mixture is enough to entirely blacken the paste. This is, like chromic acid and ether (see note 8), a very sensitive reagent (test) for peroxide of hydrogen.

are so characteristic of hydrogen peroxide as a substance which is unstable and easily decomposable with the evolution of heat, must be referred the following: in the presence of many substances containing oxygen it evolves not only its own oxygen, but also that of the substances which are brought into contact with it—that is, **it acts in a reducing manner**. It behaves thus with the oxides of silver, mercury, gold, and platinum, lead dioxide, &c. The oxygen in these substances is not stable, and therefore the feeble influence of contact is enough to destroy its position. Hydrogen peroxide, especially in a concentrated form, in contact with these substances, evolves an immense quantity of oxygen, so that an explosion takes place, and an exceedingly powerful evolution of heat is observed if hydrogen peroxide in a concentrated form be made to drop upon these substances in the form of dry powder. The decomposition also proceeds with dilute solutions,²⁷ but more slowly.

Just as a whole series of saltlike compounds, especially the oxides, hydrates, and salts, correspond with water, so also there are many substances analogous to hydrogen peroxide. Thus, for instance, calcium peroxide is related to hydrogen peroxide in exactly the same way as calcium oxide or lime is related to water. In both cases the hydrogen is replaced by calcium.^{27a} But it is particularly instructive

²⁷ To explain the phenomenon, Brodie, Clausius, and Schönbein suppose ordinary oxygen to be an electrically neutral substance, composed, so to speak, of two oppositely electrified kinds of oxygen—positive and negative. It is supposed that hydrogen peroxide contains one kind of such polar oxygen, whilst in the oxides of the above-named metals the oxygen is of opposite polarity. It is further supposed that in the oxides of the metals the oxygen is electro-negative, and in hydrogen peroxide electro-positive, and that on the mutual contact of these substances ordinary neutral oxygen is evolved as a consequence of the mutual attraction of the oxygens of opposite polarity. Brodie admitted the polarity of oxygen in combination, but not in an uncombined state, whilst Schönbein supposes uncombined oxygen to be polar also and regards ozone as electro-negative oxygen. The supposition that the oxygen of ozone is different from that of hydrogen peroxide is contradicted by the fact that in acting on barium peroxide strong sulphuric acid forms ozone, and dilute acid forms hydrogen peroxide.

^{27a} It should be mentioned that Schiloff (1893) on taking a 3 per cent. solution of H_2O_2 , adding soda to it, and then extracting the peroxide of hydrogen from the mixture by shaking it with ether, obtained a 50 per cent. solution of H_2O_2 , which, although perfectly free from other acids, gave a **distinctly acid reaction** with litmus. And here attention should first of all be turned to the fact that the peroxides of the metals correspond with H_2O_2 , like salts with an acid, for instance, Na_2O_2 and BaO_2 , &c. Furthermore, it must be remembered that O is an analogue of S (Chaps. XV. and XX.), and sulphur gives H_2S , H_2SO_3 , and H_2SO_4 . And sulphurous acid, H_2SO_3 , is unstable as a hydrate, and forms water and the anhydride SO_2 . If the sulphur be replaced by oxygen, then instead of H_2SO_3 and SO_2 , we have H_2OO_3 and OO_2 . The latter is ozone, while K_2O_4 (peroxide of potassium) corresponds with the hydrate H_2O_4 as with an acid. And between H_2O and H_2O_4 there may exist intermediate compounds, the first of which would be H_2O_2 , in which, from analogy to the sulphur compounds, one would expect acid properties. Besides which we may mention that for sulphur, besides H_2S (which is a

to remark that the nearest approach to the properties of hydrogen peroxide is afforded by a non-metallic element, chlorine, which, in its action on colouring matters, its capacity for oxidising and for evolving oxygen from many oxides, exhibits behaviour analogous to that of hydrogen peroxide. Even the very formation of chlorine is closely analogous to the formation of peroxide of hydrogen; chlorine is obtained from manganese peroxide (dioxide), MnO_2 , and hydrochloric acid, HCl , and hydrogen peroxide from barium peroxide (dioxide), BaO_2 , and the same acid. The result in one case is essentially water, chlorine, and manganese chloride; and in the other case, barium chloride and hydrogen peroxide are produced. Hence water + chlorine corresponds with hydrogen peroxide, and the action of chlorine in presence of water is analogous to the action of hydrogen peroxide. This analogy between chlorine and hydrogen peroxide is expressed in the conception of an aqueous radicle, which (Chapter III.) has already been mentioned. **This aqueous radicle** (or hydroxyl, HO) is that which is left if water be imagined to be deprived of half of its hydrogen. According to this method of expression, caustic soda will be a compound of sodium with the aqueous radicle, because it is formed from water with the evolution of half the hydrogen. This is expressed by the following formulæ: water, H_2O or HHO and caustic soda, NaHO , just as hydrochloric acid is HCl and sodium chloride NaCl . Hence the aqueous radicle HO is a compound radicle, just as chlorine, Cl , is a simple radicle. They both

feeble acid), H_2S_2 , H_2S_3 , H_2S_5 are known. Thus, in many respects, H_2O_2 offers points of resemblance to acid compounds, and, as regards its qualitative (reactive) analogies, it not only resembles Na_2O_2 , BaO_2 , &c., but also persulphuric acid HSO_4 (to which the anhydride S_2O_7 corresponds), &c., which will be subsequently described. And here we may add, respecting the now vast class of per-compounds, (*a*) that they are formed under the same conditions as peroxide of hydrogen (for instance, by electrolysis, at the anode) or by its double decomposition or combination; (*b*) that elements like S , C , &c., which give acids, are able to form per-compounds or per-acids, which in their turn form salts with the alkalis; for instance, per-sulphuric acid; (*c*) that metals like molybdenum, vanadium, &c., which give higher acid oxides, R_2O_n , are usually able also to form per-acids corresponding with the higher oxides and oxygen; (*d*) that metals giving bases R_2O_n are often able also to form peroxides, containing a further amount of oxygen; for instance, sodium, barium, &c.; but these peroxides, while able to combine with other peroxides and per-acids, are apparently unable to give salts with ordinary acids; and (*e*) all such per-compounds are able to give peroxide of hydrogen, to the reactions of which their own are similar. Prof. P. G. Melikoff (Odessa) has done much work on the per-compounds of different elements, and has arrived at the following conclusions (1902): 1. The elements of high atomic weights belonging to the even series form per-acids by the action of H_2O_2 . 2. Among the typical elements (see Chap. XV.), only boron forms a per-acid by the action of H_2O_2 . 3. The typical elements, having acid properties (for instance, C , N), only form salts of the per-acids by electrolysis. Per-compounds are formed by the action of H_2O_2 on salts as well as on bases and acids. For instance, Kazanetsky showed that potash, K_2CO_3 , is able to form with H_2O_2 a saline compound, in which the excess of oxygen must be regarded as united, not to the basic or acid oxide, but to the salt formed by them, or else that H_2O_2 is able to attach itself to entire molecules like water of crystallisation.

give hydrogen compounds, HHO, water, and HCl, hydrochloric acid; sodium compounds, NaHO and NaCl, and a whole series of analogous compounds. Free chlorine in this sense will be ClCl, and hydrogen peroxide HOHO, which indeed expresses its composition, because it contains twice as much oxygen as water does.²⁸

Thus in ozone and hydrogen peroxide we see examples of very unstable, easily decomposable (in time spontaneously, and on contact) substances, full of the energy necessary for change,^{28a} capable of being easily reconstituted (in this case decomposing with the evolution of heat); they are therefore examples **of unstable chemical equilibria**. If a substance exists, it signifies that it already presents a certain form of equilibrium between those elements of which it is built up. But chemical, like mechanical, equilibria exhibit different degrees of stability or solidity.²⁹

Besides this, hydrogen peroxide presents another side of the subject which is none the less clear and of general importance.

Hydrogen unites with oxygen in two degrees of oxidation: water

²⁸ Tamman and Carrara showed, by determining the depression (fall of the temperature of the formation of ice, Chapters I. and VII.), that the molecule of peroxide of hydrogen contains H_2O_2 , and not HO or H_3O_3 .

^{28a} The lower oxides of nitrogen and chlorine and the higher oxides of manganese are also formed with the absorption of heat, and therefore, like hydrogen peroxide, act in a powerfully oxidising manner, and are not formed by the same methods as the majority of other oxides. It is evident that, being endowed with a richer store of energy (acquired in combination or by absorption of heat), such substances, compared with others poorer in energy, will exhibit a greater diversity of chemical action with other substances.

²⁹ If the point of support of a body lies in a vertical line below the centre of gravity, it is in unstable equilibrium. If the centre of gravity lies below the point of support, the state of equilibrium is very stable, and a vibration may take place about this position of stable equilibrium, as in a pendulum or balance, where the body finally assumes a position of stable equilibrium. But if, keeping to the same mechanical example, the body be supported, not on a point, in the geometrical sense of the word, but on a small plane, then the state of unstable equilibrium may be preserved, unless destroyed by external influences. Thus a man stands upright supported on a plane, or on several points of the surfaces of his feet, having the centre of gravity above the points of support. Vibration is then possible, but it is limited, otherwise on passing outside the limit of possible equilibrium another more stable position is obtained, about which vibration becomes more possible. A prism immersed in water may have several more or less stable positions of equilibrium. The same is also true with the atoms in molecules. Some molecules present a state of more stable equilibrium than others. Hence, from this simple comparison, it will be at once evident that the stability of molecules may vary considerably; that one and the same elements, taken in the same number, may give isomerides of different stability; and, lastly, that there may exist states of equilibria which are so unstable, so ephemeral, that they will only arise under particularly special conditions—such, for example, as certain hydrates mentioned in the first chapter (see notes 57, 67, and others). And if in one case the instability of a given state of equilibrium is expressed by its instability with a change of temperature or physical state, it is in other cases expressed by the facility with which it decomposes under the influence either of contact or of the chemical influence of other substances.

or hydrogen oxide, and oxygenated water or hydrogen peroxide; for a given quantity of hydrogen, the peroxide contains twice as much oxygen as does water. This is a fresh example confirming the correctness of the law of multiple proportions, to which we have already referred in speaking of the water of crystallisation of salts. We can now formulate this law—the **law of multiple proportions**. *If two substances A and B (either simple or compound) unite together to form several compounds, A_nB_m , A_qB_r , . . ., then, having expressed the compositions of all these compounds in such a way that the quantity (by weight or volume) of one of the component parts is a constant quantity A, it will be observed that in all the compounds AB_m , AB_b , . . . the quantities of the other component part, B, will always be in commensurable relations, generally in simple multiple proportion—that is, that $a : b$. . . (or m/n is to r/q) can be expressed as the ratio of simple whole numbers; for instance, as 1 : 2, 2 : 3, or 3 : 4. . . .*

The analysis of water shows that in 100 parts by weight it contains 11.19 parts by weight of hydrogen and 88.81 of oxygen, and the analysis of peroxide of hydrogen shows that it contains 94.07 parts of oxygen to 5.93 parts of hydrogen. Here the analyses are expressed, as they generally are, in percentages; that is, they give the amounts of the elements in a hundred parts by weight of the substance. The direct comparison of the percentage compositions of water and hydrogen peroxide does not reveal any simple relation. But such a relation is immediately apparent if we calculate the compositions of water and hydrogen peroxide, taking either the quantity of oxygen or the quantity of hydrogen as a constant quantity—for instance, unity. The proportions show that in water there are contained eight parts of oxygen to one part of hydrogen, and in hydrogen peroxide sixteen parts of oxygen to one part of hydrogen; or one-eighth part of hydrogen in water and one-sixteenth part of hydrogen in hydrogen peroxide to one part of oxygen. Naturally, the analysis does not give these figures with absolute exactness—it gives them within a certain degree of error—but they approximate, as the error diminishes, to the limit 1 : 2 here given.

An exactly similar multiple proportion is observed in the composition of all other well-investigated definite chemical compounds,³⁰

³⁰ When, for example, any element forms several oxides, these are subject to the law of multiple proportions. For a given quantity of the non-metal or metal the quantities of oxygen in the different degrees of oxidation will stand as 1 : 2, or as 1 : 3, or as 2 : 3, or as 2 : 7, and so on. Thus, for instance, copper combines with oxygen in at least two proportions, forming the oxides found in nature, and called the suboxide and the oxide of copper, Cu_2O and CuO ; the oxide contains twice as much oxygen as the suboxide. Lead also presents two degrees of oxidation, the oxide and dioxide, and in the latter

and therefore the law of multiple proportions is accepted in chemistry as the starting-point from which other considerations proceed.

The law of multiple proportions was discovered at the beginning of the last century by **John Dalton**, of Manchester, in investigating the compounds of carbon with hydrogen. It appeared that two gaseous compounds of these substances—marsh gas, CH_4 , and olefiant gas, C_2H_4 , contain, for one and the same quantity of hydrogen, quantities of carbon which stand in multiple proportion, marsh gas containing relatively half as much carbon as olefiant gas. Although the analysis of that time was not exact, still the accuracy of this law, recognised by Dalton, was confirmed by later and more accurate investigations. On establishing the law of multiple proportions, Dalton gave a hypothetical explanation for it. This explanation is based on the atomic theory of matter. In fact, the law of multiple proportions may be very easily understood by admitting the atomic structure of matter.

The **essence of the atomic theory** is that matter is supposed to consist of an agglomeration of small and indivisible (by natural forces) parts—atoms—which do not fill up the whole space occupied by a substance, but stand apart from each other, as the sun, planets, and stars do not fill up the whole space of the universe, but are at a distance from each other.^{30a} The form and properties of substances are deter-

there is twice as much oxygen as in the former, the formulæ being PbO and PbO_2 . When a base and an acid are capable of forming several kinds of salts, normal, acid, basic, and anhydro-, it is found that these also clearly exemplify the law of multiple proportions. This was demonstrated by Wollaston soon after the discovery of the law in question. We saw in the first chapter that salts show different degrees of combination with water of crystallisation, and that these obey the law of multiple proportions. By endeavouring in Chap. I. to prove hypothetically that in solutions we have nothing else but the liquid products of the dissociation of definite hydrates which are subject to the law of multiple proportions, it is my aim to bring also this class of indefinite compounds under the general principle enunciated by Dalton; just as astronomers have discovered a proof and not a negation of the laws of Newton in the phenomena known as perturbations.

^{30a} I have no doubt that the atomic theory, so steadfastly applied, after its adoption in chemistry, to all natural science in the nineteenth century, has its philosophical defects proper to materialism. Yet it cannot be denied that atomism presents a sublime generalisation in harmony with the fundamental principles of philosophy, for it directly assimilates the structure of the universe (in the form in which it has been revealed by the conquests of astronomy—consisting of solitary suns and planets separated by space but united by reacting forces), to the structure of matter out of atoms, and by so doing greatly facilitates the comprehension of things and phenomena. According to this view, a molecule of matter is as complex as an entire universe, and it contains its solitary bodies—atoms—maintained, like the suns and planets, by their proper forces in mobile but stable equilibrium, its systems, &c. One of the merits of atomism is that it has brought the infinitely small into harmony with the infinitely great, and by so doing has gained new life. The natural philosophy of modern times has the further merit over that of former ages, that it no longer regards man as the pivot of the universe, but consciously submits itself to harmonious, coherent, and logical laws embracing all time

mined by the positions of their atoms in space and by their state of motion, whilst the reactions accomplished by substances are regarded as redistributions of the relative positions of atoms and as changes in their motion. The atomic representation of matter arose in very ancient times,³¹ and until recently was at variance with the dynamical

and space and extending alike over the immensity of the heavens and the infinitesimal atom. The radical defect of modern atomism, I think, lies in the vagueness of the conception of the 'ether' filling both interplanetary and interatomic space, but in directing its chief attention to the investigation of phenomena which take place in 'ether' (electric, luminiferous, &c.), modern science is, I think, following the right direction for revealing the hidden mysteries of nature. Modern science endeavours to, but cannot yet clearly, interpret by means of ether, as a substance material, though imponderable and chemically active, yet not giving chemically ponderable bodies. This is one of the problems of science which have been bequeathed to us by the nineteenth century.

³¹ Leucippus, Democritus, and especially Lucretius, in the classical ages, represented matter as made up of atoms—that is, of parts incapable of further division. The geometrical impossibility of such an admission, as well as the conclusions which were deduced by the ancient atomists from their fundamental propositions, prevented other philosophers from following them, and the atomic doctrine, like very many others, lived in the imaginations of its followers without being ratified by fact. Between the present atomic theory and the doctrine of the above-named ancient philosophers there is naturally a remote historical connection, as between the doctrines of Pythagoras and Copernicus, but they are essentially different. For us the atom is indivisible, not in the geometrical abstract sense, but only in a physical and chemical sense. It would be better to call the atoms indivisible **individuals**. The Greek 'atom' corresponds with the Latin 'individual,' both according to the etymology and original sense of the words, but in course of time these two words have acquired a different meaning. The 'individual' is mechanically and geometrically divisible, and only indivisible in a special sense. The earth, the sun, a man, and a fly are individuals, although geometrically divisible. Thus the 'atoms' of contemporary science, indivisible in a chemical sense, form those units with which we are concerned in the investigation of the natural phenomena of matter, just as a man is an indivisible unit in the investigation of social relations, or as the stars, planets, and luminaries serve as units in astronomy. The formation of the vortex hypothesis, in which, as we shall afterwards see, atoms are entire whirls, mechanically complex, although physico-chemically indivisible, clearly shows that the scientific men of our time, in holding to the atomic theory, have only borrowed the word and form of expression from the ancient philosophers, and not the essence of their atomic doctrine. It is erroneous to imagine that the contemporary conceptions of the atomists are nothing but the repetition of the metaphysical reasonings of the ancients. To show the true meaning of the atomism of the ancient philosophers, and the profound difference between their points of argument and those of contemporary men of science, I cite the following fundamental propositions of Democritus (B.C. 470–380) as the best expounder of the atomic doctrine of the ancients:—

- (1) Nothing can proceed from nothing, nothing that exists (and hence matter) can disappear or be destroyed, and every change consists only of a combination or separation.
- (2) Nothing is accidental, there is a reason and necessity for everything.
- (3) All except atoms and vacua is reason and not existence.
- (4) The atoms, which are infinite in number and form, constitute the visible universe by their motion, impact, and consequent revolving motion.
- (5) The variety of objects depends only upon a difference in the number, form, and order of the atoms of which they are formed, and not upon a qualitative difference of their atoms, which only act upon each other by pressure and impact.
- (6) The spirit, like fire, consists of minute spherical, smooth, and very mobile and all-penetrating atoms, whose motion forms the phenomenon of life.

These Democritan, chiefly metaphysical, principles of atomism are so essentially different from the principles of the present atomic doctrine, which is exclusively applied to explaining the

hypothesis, which considers matter as only a manifestation of forces. At the present time, however, the great majority of scientific men uphold the atomic hypothesis, but the present conception of an atom is quite different from that of the ancient philosophers. An atom at the present day is regarded rather as an ultimate, measurable individual or unit, which is indivisible by physical ³² and chemical forces, whilst the

phenomena of the external world, that it may be useful to mention the essence of the atomic propositions of Boscovitch, a Slav who lived in the middle of the eighteenth century, and who is regarded as the founder of the modern atomic doctrines, which, however, did not take hold upon the minds of scientific men, and were rarely applied, prior to the time of Dalton—i.e., until the beginning of the nineteenth century. The **doctrine of Boscovitch** was enunciated by him in 1758–1764 in his *Philosophiæ naturalis theoria reducta ad unicam legem virium in natura existentium*. Boscovitch considers matter to be composed of atoms, and the atoms to be the points or centres of forces (just as the stars and planets may be considered as points of space), acting between bodies and their parts. These forces vary with the distance, so that beyond a certain very small distance all atoms, and hence also their aggregates, are attracted according to Newton's law, but at less distances, wavelike spheres of gradually decreasing attraction and increasing (as the distance decreases) repulsion alternate, until at last at a minimum distance only the repellent action remains. Atoms, therefore, cannot merge into each other. Consequently, the atoms are held at a certain distance from each other, and therefore occupy space. Boscovitch compares the spheres of repulsion surrounding the atoms to the spheres of action of firing of a detachment of soldiers. According to his doctrine, atoms are indestructible, do not merge into each other, have mass, and are everlasting and mobile under the action of the forces proper to them. Maxwell rightly calls this hypothesis the 'extreme' among those existing to explain matter, but many aspects of Boscovitch's doctrine repeat themselves in the views of our day, with this essential difference, that instead of a mathematical point furnished with the properties of mass, the atoms are endowed with a corporality, just as the stars and planets are corporal, although in certain aspects of their interaction they may be regarded as mathematical points. In my opinion, the atomism of our day must first of all be regarded merely as a convenient method for the investigation of ponderable matter, a working hypothesis. As a geometrician in reasoning about curves represents them as formed of a succession of straight lines, because such a method enables him to analyse the subject under investigation, so the scientific man applies the atomic theory as a means of analysing the phenomena of nature. Naturally there are people now, as in ancient times, and as there always will be, who apply reality to imagination, and therefore there are to be found atomists of extreme views; but it is not in their spirit that we should acknowledge the great services rendered to all science by the atomic doctrine, which, while it has been essentially independently developed, is, if it be desired to reduce all ideas to the teachings of the ancients, a union of the ancient dynamical and atomic doctrines.

³² Dalton and many of his successors distinguished the atoms of elements and compounds, in which they clearly symbolised the difference between their opinion and the representations of the ancients. At the present time, only the individual particles of the elements, indivisible by physical and chemical forces, are termed atoms, while those of compounds indivisible under physical changes are termed molecules: these latter are divisible into atoms by chemical forces. But the atoms of simple bodies according to many contemporary men of science (Crookes, J. Thomson, Lord Kelvin, and others, especially among the English) split up, under certain circumstances, into primary infinitesimal parts (electrons, radiant matter, &c.), which clearly proves that many now consider the atom to be divisible. But here we stand evidently on the very limits of contemporary knowledge, and I therefore think it my duty to advise the beginner to

atom of the ancients was indivisible even in a geometrical sense, that is, infinitely small. When **Dalton** (1804) discovered the law of multiple proportions, he pronounced himself in favour of the atomic doctrine, because it enables this law to be very easily understood. If the divisibility of every element has a limit, namely, the atom, then the atoms of elements are the extreme limits of all divisibility, and if they differ from each other in their nature, the formation of a compound from elementary matter must consist in the aggregation of several different atoms into one whole or system of atoms, now termed **particles or molecules**. As atoms can only combine in a system in their entire masses, it is evident that not only the law of definite composition, but also that of multiple proportions, must apply to the combination of atoms with one another; for one atom of a substance can combine with one, two, or three atoms of another substance, or in general one, two, or three atoms of one element are able to combine with one, two, or three atoms of another, this being the essence of the law of multiple proportions. Many chemical and physical data are well explained by the aid of the atomic theory. The displacement of one element by another follows the law of equivalence. In this case one or several atoms of a given element take the place of one or several atoms of another element in its compounds. The atoms of different substances can be mixed together in the same sense as sand can be mixed with clay. They do not unite into one whole—i.e., there is not a perfect blending in the one or the other case, but only a juxtaposition, a homogeneous whole being formed from individual parts. This is the first and most simple method of applying the atomic theory to the explanation of chemical phenomena.³³

refrain from this province of thought, for there is here much that is possible, but nothing certain.

³³ In the present condition of science, either the atomic or the dynamical hypothesis is inevitably obliged to admit the existence of an invisible and imperceptible motion in matter, without which it is impossible to understand either light or heat, gaseous pressure, or any of the mechanical, physical, or chemical phenomena. The ancients saw vital motion in animals only, but to us the smallest particle of matter, endowed with *vis viva*, or energy in some degree or other, is incomprehensible without self-existent motion. Thus motion has become a conception inseparably knit with the conception of matter, and this has prepared the ground for the revival of the dynamical hypothesis of the constitution of matter. In the atomic theory there has arisen that generalising idea by which the world of atoms is constructed, like the universe of heavenly bodies, of its suns, planets, and meteors, endowed with everlasting force of motion and forming molecules, just as the heavenly bodies form systems like the solar system; and these molecules are only relatively indivisible in the same way as the planets of the solar system are inseparable, and are stable and lasting like the solar system. Such a representation, without necessitating the absolute indivisibility of atoms, expresses all that science can require for a hypothetical representation of the constitution of matter. In closer proximity to the dynamical hypothesis of the constitution of matter is the oft-times revived **vortex**

A certain number of atoms n of an element A in combining with several atoms m of another element B give a compound A_nB_m , each

hypothesis. Descartes first endeavoured to develop it, while Helmholtz and Thomson (Lord Kelvin) gave it a fuller and more modern form and many scientific men applied it to physics and chemistry. The idea of vortex rings serves as the starting-point of this hypothesis; these are familiar to all in the rings of tobacco smoke, and may be artificially obtained by giving a sharp blow to the sides of a cardboard box having a circular orifice and filled with smoke. Phosphoretted hydrogen, as we shall see later on, when bubbling from water always gives very perfect vortex rings in a still atmosphere. In such rings it is easy to observe a constant circular motion about their axes, and to notice the stability the rings possess in their motion of translation. This unchangeable mass, endowed with a rapid internal motion, is likened to the atom. In a medium deprived of friction, such a ring, as is shown by a theoretical consideration of the subject from a mechanical point of view, would be perpetual and unchangeable. The rings are capable of grouping together, and in combining, without being absolutely indivisible, they do not break up into parts. The vortex hypothesis has been established in our times, but it has not been fully developed; it can be applied to the explanation of chemical phenomena, although not readily; it tells us nothing of the nature of the space existing between the rings (just as it is not clear what exists between atoms and between the planets), neither does it tell us what is the nature of the moving substance of the ring, and therefore for the present it only presents the germ of a hypothetical conception of the constitution of matter; consequently I consider that it would be superfluous to speak of it in greater detail.

However, the thoughts of investigators are now (and naturally will be in the future), as they were in the time of Dalton, often turned to the question of the limitation of the mechanical division of matter, and the atomists have searched for an answer in the most diverse spheres of nature. In order to show how closely all the provinces of natural science are bound together, I select one of the methods of attacking this problem which does not in any way refer to chemistry.

Wollaston suggested investigating the **atmosphere of the heavenly bodies** as a means for confirming the existence of atoms. If the divisibility of matter be infinite, then air must extend throughout the entire space of the heavens, just as it extends all over the earth by virtue of its elasticity and diffusion. If the infinite divisibility of matter be admitted, it is impossible that any portion of the whole space of the universe can be entirely void of the component parts of our atmosphere. But if matter be divisible down to a certain limit only—namely, down to the atom—then there *can exist* a heavenly body void of an atmosphere; and if such a body be discovered, it would serve as an important factor in determining the validity of the atomic doctrine. The moon has long been regarded as such a luminary, and on this account, and especially because of its proximity to the earth, has been cited as the best proof of the validity of the atomic doctrine. This proof is apparently (Poisson) deprived of some of its force by the possibility of the transformation of the component parts of our atmosphere into a solid or liquid state at immense heights above the earth's surface, where the temperature is exceedingly low; but a series of researches (Pouillet) has shown that the temperature of the heavenly space is comparatively not so very low, and is attainable by experimental means, so that at the low existing pressure the liquefaction of the gases of the atmosphere cannot be expected even on the moon. Hence the absence of an atmosphere about the moon, if it were not subject to doubt, would be counted a forcible proof of the atomic theory. As a proof of the absence of a lunar atmosphere, it is cited that the moon, in its independent motion between the stars, when eclipsing a star—that is, when passing between the eye and the star—does not show any signs of refraction at its edge; the image of the star does not alter its position in the heavens on approaching the moon's surface; consequently there is no atmosphere on the moon's surface capable of refracting light rays. It is on this that the proof of the absence of a lunar atmosphere is based. But this is a very weak proof, and there are even facts which are in exact contradiction to it, and by

molecule of which will contain the atoms of the elements A and B in this ratio, and therefore the compound will present a **definite composition**, expressed by the formula A_nB_m , where A and B are the weights of the atoms, and n and m their relative numbers. If the same elements A and B, in addition to A_nB_m , also yield another compound A_rB_q , then by expressing the composition of the first compound by $A_{nr}B_{mr}$ (and

means of which the existence of a lunar atmosphere may be proved. The entire surface of the moon is covered with a number of mountains, having, in the majority of cases, the conical form natural to volcanoes. The volcanic character of the lunar mountains was confirmed in October 1866, when a change was observed in the form of one of them (the crater Linnea). These mountains must be on the edge of the lunar disc. Seen in profile they screen one another and interfere with observations on the surface of the moon, so that when looking at the edge of the lunar disc we are obliged to make our observations not on the moon's surface, but at the summits of the lunar mountains. These mountains are higher than those on our earth, and consequently at their summits the lunar atmosphere must be exceedingly rarefied, even if it possess an observable density at the surface. Knowing the mass of the moon to be eighty-two times less than that of the earth, we are able to show that our atmosphere at the moon's surface would be about twenty-eight times lighter than it is on the earth, and consequently at the very surface of the moon the refraction of light by the lunar atmosphere must be very slight, whilst at the heights of the lunar mountains it must be imperceptible, and would be lost within the limits of experimental error. So that the absence of refraction of light at the edge of the moon's disc cannot as yet be urged in proof of the absence of a lunar atmosphere. There is even a series of observations obliging us to admit the existence of such an atmosphere. These researches are due to Sir John Herschel. This is what he writes: 'It has often been remarked that during the eclipse of a star by the moon there occurs a peculiar optical illusion; it seems as if the star before disappearing passed over the edge of the moon and is seen through the lunar disc, sometimes for a fairly long period of time. I myself have observed this phenomenon, for the occurrence of which there is perfectly trustworthy evidence. I ascribe it to optical illusion; but it must be admitted that the star might have been seen on the lunar disc through some deep ravine on the moon.' Geniller, in Belgium (1856), following the opinion of Cassini, Euler, and others, gave an explanation of this phenomenon: he considers it due to the refraction of light in the valleys of the lunar mountains which occur on the edge of the lunar disc. In fact, although these valleys do not probably present the form of straight ravines, yet it may sometimes happen that the light of a star is so refracted that its image might be seen, notwithstanding the absence of a direct path for the light-rays. He then goes on to remark that the density of the lunar atmosphere must be variable in different parts owing to the very long nights on the moon. On the dark, or non-illuminated portion, owing to the long nights, which last thirteen of our days and nights, there must be excessive cold, and hence a denser atmosphere, whilst, on the contrary, on the illuminated portion the atmosphere must be much more rarefied. This variation in the temperature of the different parts of the moon's surface explains also the absence of clouds, notwithstanding the possible presence of air and aqueous vapour, on the visible portion of the moon. The presence of atmospheres round the sun and planets, judging from astronomical observations, may be considered as fully proved. On Jupiter and Mars bands of clouds may even be distinguished.

Thus the atomic doctrine, admitting only a finite mechanical divisibility, must be, as yet at least, accepted merely as a means, similar to that which a mathematician employs when he breaks up a continuous curvilinear line into a number of straight lines. There is a simplicity of representation in atoms, but there is no absolute necessity to have recourse to them. The conception of the individuality of the parts of matter exhibited in chemical elements is alone necessary and certain.

this is the same composition as A_nB_m), and that of the second compound by $A_{rn}B_{qn}$, we have the law of multiple proportions, because for a given quantity of the first element, A_{rn} , there occur quantities of the second element bearing the same ratio to each other as mr bears to qn ; and as m , r , q , and n are whole numbers, their products are also whole numbers, and it is this that is expressed by the law of multiple proportions. Consequently the atomic theory is in accordance with and evokes the first laws of definite chemical compounds: the law of definite composition and the law of multiple proportions.

The same thing is seen in the relation of the atomic theory to the third law of definite chemical compounds—the **law of reciprocal combining weights**—which is as follows:—If a certain weight of a substance C combine with a weight a of a substance A, and with a weight b of a substance B, then, also, the substances A and B will combine together in quantities a and b (or in multiples of them). This follows at once from our conception of atoms. Let A, B, and C be the weights of the atoms of the three elements, and for simplicity of reasoning let us suppose that combination takes place between single atoms. It is evident that if the element C gives AC and BC, then the elements A and B will give a compound AB, or A_nB_m . And this is what we really find in nature. Sulphur combines with hydrogen and with oxygen. Sulphuretted hydrogen contains thirty-two parts by weight of sulphur to every two parts by weight of hydrogen; this is expressed by the formula H_2S . Sulphur dioxide, SO_2 , contains thirty-two parts of sulphur and thirty-two parts of oxygen, and therefore we conclude, from the law of combining weights, that oxygen and hydrogen will combine in the proportion of two parts of hydrogen and thirty-two parts of oxygen, or in some multiples of these numbers. And we have seen this to be the case. Hydrogen peroxide contains thirty-two parts of oxygen, and water sixteen parts, to every two parts of hydrogen; and so it is in all other cases. This consequence of the atomic theory is in accordance with nature and with the results of analysis, and is one of the most important laws of chemistry. It is a law, because it indicates the *relation between* the weights of substances entering into chemical combination. Further, it is an eminently exact law, and not an approximate one. The law of combining weights is a law of nature, and by no means an hypothesis, for even if the entire theory of atoms be refuted, the laws of multiple proportions and of combining weights will still remain, inasmuch as they are the expression of facts. They may be foreseen from the atomic theory, and historically the law of combining weights is intimately connected with this theory; they are, however, not identical, but only connected, with it. The law of com-

binning weights is formulated with great ease, and is an immediate consequence of the atomic theory, without which it would be difficult to understand. Data for its evolution existed previously, but it was not formulated until those data were interpreted by the atomic theory, an hypothesis which up to the present time has contradicted neither experiment nor fact, and is useful and of general application. Such is the nature of hypotheses. They are indispensable to science; they bestow an order and simplicity which are only attainable with difficulty without their aid. The whole history of science is a proof of this. And it may therefore be truly said that it is better to hold to an hypothesis which may afterwards prove untrue than to have none at all. Hypotheses facilitate scientific work and render it consistent. Like the plough of the husbandman, they help forward the work of the labourer in the search for truth.

CHAPTER V

NITROGEN AND AIR

ALTHOUGH oxygen is chemically the most active component of the atmosphere surrounding us, nitrogen forms the greater part of it by weight and by volume, and indeed constitutes over three-quarters (by volume) of the atmosphere; and as **nitrogen** is only slightly lighter than oxygen, it forms about three-quarters of the air by weight also. While entering in so considerable a quantity into the composition of air, nitrogen does not seem to play any active part in the atmosphere, the chemical action of which is mainly dependent on the oxygen it contains. But a correct idea of the part played by the nitrogen in the air can only be formed when we have learnt that animals cannot exist in pure oxygen, but pass into an abnormal state, and even die; and that the nitrogen of the air, although slowly, forms numerous compounds, many of which play a most important part in nature, especially in the life of organisms. Plants, and especially animals, besides requiring free oxygen, are absolutely dependent upon nitrogenous compounds for their nutrition, because these form their most chemically active components. However, neither plants¹ nor animals directly absorb the gaseous nitrogen of the air, but take it up from ready-formed nitrogenous compounds; further, plants are nourished by the nitrogenous substances contained in the soil and water, and animals by the nitrogenous substances contained in plants and in other animals. Atmospheric electricity is capable of aiding the passage of gaseous nitrogen into nitrogenous compounds, as we shall afterwards see, and the resultant substances are carried to the soil by rain, and there serve for the nourishment of plants. Plentiful harvests, fine crops of hay, vigorous growth of trees—other conditions being equal—are only obtained when the soil contains **ready-formed nitrogenous compounds**, consisting either of those which occur in air and water, or of the residues of the decomposition of other plants or animals (as in manure). The nitrogenous substances contained in animals have their

¹ See note 15^a.

origin in those substances which are formed in plants. Thus the nitrogen of the atmosphere is the origin of all the nitrogenous substances occurring in animals and plants, although not directly so, but only after first combining with the other elements of air.

The nitrogenous compounds which enter into the composition of plants and animals are of primary importance ; no vegetable or animal cell—that is, the elementary form of organism—exists without containing a nitrogenous substance, and, moreover, the life of the organism manifests itself primarily in these nitrogenous substances. The germs, seeds, and those parts by which cells multiply abound in nitrogenous substances ; the sum total of the phenomena which are proper to organisms depends primarily on the chemical properties of the readily changeable complex (albuminous) nitrogenous substances which enter into their composition. It will be sufficient, for instance, to point out the fact that vegetable and animal organisms, clearly distinguishable as such, are characterised by the different degrees of energy they manifest, and at the same time by a difference in the amounts of nitrogenous substances they contain. In plants, which compared with animals possess but little activity, being incapable of independent movement, &c., the proportion of nitrogen is very much less than in animals, whose tissues are almost exclusively formed of nitrogenous substances. It is remarkable that the nitrogenous parts of plants, chiefly of the lower orders, sometimes present both forms and properties resembling those of animal organisms ; this is seen, for example, in the zoospores of seaweeds, or those parts by means of which the latter multiply themselves. On leaving the seaweed these zoospores resemble in many respects the lower orders of animal life, having, like the latter, the property of motion. They also approach the animal kingdom in their composition, their outer coating containing nitrogenous matter. Directly the zoospore becomes covered with that non-nitrogenous or cellular coating which is proper to all the ordinary cells of plants, it loses all resemblance to an animal organism and becomes a small plant. It may be thought from this that the cause of the difference between the vital processes of animals and those of plants lies in the different amounts of nitrogenous substances they contain. The nitrogenous substances which occur in plants and predominate in animals belong to a series of exceedingly complex and very changeable chemical compounds ; their elementary composition alone shows this, for besides nitrogen they contain carbon, hydrogen, oxygen, and sulphur. Being distinguished by a very great instability under many conditions in which other compounds remain unchanged, these substances are fitted for those perpetual and regular changes which form the first condition

of vital activity. These complex and changeable nitrogenous substances of the organism are called **proteid substances**. The white of eggs is a familiar example of such substances. They are also contained in the tissues of the flesh of animals, the curdy elements of milk, the glutinous matter of wheaten flour, or so-called gluten, which forms the chief component of macaroni, &c.

Nitrogen occurs in the earth's crust, in compounds either forming the remains of plants and animals, or derived from the nitrogen of the atmosphere as a consequence of its combination with the other component parts of the air. It is not found in other forms in the earth's crust; so that nitrogen must be considered, in contradistinction to oxygen, as an element which is purely superficial, and extends hardly at all to the depths of the earth.^{1a}

Nitrogen is liberated in a free state in the decomposition—for example, by combustion—of the **nitrogenous organic substances** entering into the composition of organisms. All organic substances burn when heated to redness with oxygen (or substances readily yielding it, such as oxide of copper); the oxygen combines with the carbon, sulphur, and hydrogen, and the nitrogen is evolved in a free state, because at a high temperature it forms no stable compound, but remains uncombined. Carbonic anhydride and water are formed from the carbon and hydrogen respectively, and therefore to obtain pure nitrogen it is necessary to remove the carbonic anhydride from the gaseous products obtained (after drying). This may be done very easily by the action of alkalies—for instance, caustic soda. The amount of nitrogen in organic substances is determined by a method founded on this.

It is also very easy to obtain **nitrogen from air**, because oxygen combines with many substances. Either phosphorus or metallic copper is usually employed for removing the oxygen from air, but, naturally, a number of other substances may also be used. If a small

^{1a} The reason why there are no nitrogenous substances within the earth's mass other than those which have come there with the remains of organisms, or from the air with rain-water, must be looked for in two circumstances. In the first place, in the instability of many nitrogenous compounds, which are liable to break up with the formation of gaseous nitrogen; and in the second place in the fact that the salts of nitric acid, forming the product of the action of air on many nitrogenous and especially organic compounds, are very soluble in water, and on penetrating into the depths of the earth (with water) give up their oxygen. The result of the changes of the nitrogenous organic substances which fall into the earth is without doubt frequently, if not invariably, the formation of gaseous nitrogen. Thus the gas evolved from coal always contains much nitrogen (together with marsh gas, carbonic anhydride, and other gases). The statement that a small amount of nitrogen is evolved during volcanic eruptions cannot be taken as proved, because air easily penetrates into the depths of the earth, whence it is ejected in volcanic disturbances.

saucer on which a piece of phosphorus is laid be placed on a cork floating on water, and the phosphorus be lighted, and the whole covered with a glass bell jar, the air under the jar will be deprived of its oxygen, and nitrogen alone remain; hence, on cooling, the water will rise to a certain extent in the bell jar. The same object (obtaining nitrogen from the air) is attained much more conveniently and perfectly by passing air through a red-hot tube containing copper filings. At a red heat, metallic copper combines with oxygen and gives a black powdery copper oxide. If the layer of copper be sufficiently long and the current of air slow, all the oxygen will be absorbed, and nitrogen alone will pass from the tube.²

Nitrogen may also be procured from many of its **compounds with oxygen** ³ and **hydrogen**,⁴ but the best fitted for this purpose is a saline mixture containing, on the one hand, a compound of nitrogen with oxygen, termed nitrous anhydride, N_2O_3 , and, on the other hand, ammonia (taken as a salt, Chap. VI.), NH_3 —that is, a compound of nitrogen with hydrogen. By heating such a mixture, the oxygen of the nitrous anhydride combines with the hydrogen of the ammonia, forming water, and gaseous nitrogen is evolved, $2NH_3 + N_2O_3 = 3H_2O + N_4$. Nitrogen is obtained by this method in the following manner:—A solution of caustic potash is saturated with nitrous anhydride, by which means potassium nitrite is formed, while a solution of hydrochloric acid is saturated with ammonia, by which means a saline substance called sal-ammoniac, NH_4Cl , is formed. The two solutions thus prepared are mixed together and heated. Reaction takes place according to the equation: $KNO_2 + NH_4Cl = KCl + 2H_2O + N_2$. This reaction proceeds in virtue of the fact that potassium nitrite and ammonium chloride are salts which, on interchanging their metals, give potassium chloride and ammonium nitrite, NH_4NO_2 , which breaks up into water

² In the presence of solutions of acids, copper (best as turnings, which present a large surface) absorbs oxygen at the ordinary temperature, forming CuO ; or, better still, in the presence of a solution of ammonia, when it forms a bluish-violet solution of oxide of copper in ammonia. Nitrogen is very easily procured by this method. A flask filled with copper turnings is closed with a cork furnished with a funnel and stopcock. A solution of ammonia is poured into the funnel, and caused to drop slowly upon the copper. If at the same time a current of air be passed slowly through the flask (from a gasholder), then all the oxygen will be absorbed from it and the nitrogen will pass from the flask. The gas should be washed with water to retain any ammonia that may be carried off with it.

³ The oxygen compounds of nitrogen (for example, N_2O , NO , NO_2) are decomposed at a red heat by themselves, and under the action of red-hot copper, iron, sodium, &c., they give up their oxygen to the metals, leaving the nitrogen free. According to Meyer and Langer (1885), nitrous oxide, N_2O , decomposes below 900° , although not completely

⁴ Chlorine and bromine (in excess), as well as bleaching powder (hypochlorites), take up the hydrogen from ammonia, NH_3 , leaving nitrogen. Nitrogen is best procured from ammonia by the action of a solution of sodium hypobromite on solid sal-ammoniac.

and nitrogen. This reaction does not take place without the aid of heat, but it proceeds very readily at a moderate temperature. Of the resultant substances, the nitrogen alone is gaseous. Pure nitrogen may be obtained by drying the resultant gas and passing it through a solution of sulphuric acid (to absorb a certain quantity of ammonia which is evolved in the reaction).^{4a} Before 1894, it was generally thought that nitrogen obtained from air did not differ in any way from that prepared from its compounds (after being purified); but Lord Rayleigh, in determining the weight of a known volume of nitrogen obtained by different methods, found that the nitrogen of air is almost $\frac{1}{200}$ heavier than that extracted from its compounds. Subsequently Lord Rayleigh, together with W. Ramsay, showed that the difference in density was due to the presence in the atmospheric nitrogen of a small amount of an inactive gas resembling nitrogen, which they named **argon**, and of certain other gases of which mention is made at the end of this chapter.⁵

Nitrogen is a gaseous substance which does not differ much in physical properties from air: its density, referred to that of hydrogen, is equal to 13.9—that is, it is slightly lighter than air; one litre of nitrogen weighs 1.251 gram (at 0° and 760 mm.). Nitrogen mixed with oxygen, which is slightly heavier than air, forms air. It is a gas which, like oxygen and hydrogen, is liquefied with difficulty, and is but slightly soluble in water and other liquids. Its absolute boiling-point⁵ is about -146°. Liquid nitrogen boils at -193°, its specific gravity at this temperature being about 0.89. At about -213°, in vaporising under diminished pressure, nitrogen solidifies into a colourless snow-like mass. Nitrogen does not burn,^{5a} does not support combustion, is not absorbed chemically by any of the reagents used in gas analysis, at least at the ordinary temperature—in a word, it presents a whole series of negative chemical properties. This is expressed by saying that this element has no energy for forming compounds. Although it is capable of forming compounds both with oxygen and hydrogen as well as with carbon, yet these compounds are only formed under special conditions, to which we shall turn our attention directly. At a red heat nitrogen combines with boron, titanium, silicon, barium, magnesium, and lithium,

^{4a} Ammonium nitrite may be prepared separately, only it decomposes with an explosion, and is difficult to deal with (Chap. VI. note 56).

⁵ Owing to this, nitrogen obtained from air differs slightly in some of its properties from pure nitrogen, as will be presently explained. There is no need to say that Rayleigh's and Ramsay's discoveries are among the most remarkable ever made in science, and prove to what a high degree of perfection the exact comparative investigation of substances may be brought.

^{5a} See note 11a.

forming very stable nitrogenous compounds,⁶ whose properties are entirely different from those of nitrogen compounds of hydrogen, oxygen, and carbon. However, the combination of nitrogen with carbon, although it does not take place directly between the elements at a red heat, yet proceeds with comparative ease when a mixture of charcoal with an alkaline carbonate, especially potassium carbonate or barium carbonate, is heated to redness, carbo-nitrides or cyanides of the metals being formed; for instance, $K_2CO_3 + 4C + N_2 = 2KCN + 3CO$.⁷

Nitrogen is found with oxygen in the air, but these two elements do not readily combine. Cavendish, however, in the eighteenth century, showed that **nitrogen combines with oxygen under the influence of a series of electric sparks**. Electric sparks in passing through a moist⁸ mixture of nitrogen and oxygen cause these elements to combine, forming reddish-brown fumes of oxides of nitrogen,⁹ which with water

⁶ The combination of boron with nitrogen, for instance, is accompanied by the evolution of sufficient heat to raise the mass to redness; titanium combines so easily with nitrogen that it is difficult to obtain it free from that element; lithium and magnesium easily absorb nitrogen at a red heat. It is a remarkable and instructive fact that these compounds of nitrogen are very stable and non-volatile. Carbon (C = 12) with nitrogen gives cyanogen, C_2N_2 , which is gaseous and very unstable, and the molecule of which is not large, whilst boron (B = 11) forms a nitrogenous compound which is solid, non-volatile, and very stable. Its composition, BN, is similar to that of cyanogen, but its molecular formula, B_nN_n , is probably greater. Its composition, like those of N_2Mg_3 , NNa_3 , N_2Hg_3 , and of many of the metallic nitrides, corresponds with ammonia in which all the hydrogen is replaced by a metal. A detailed study of the transformations of the nitrides now known may lead to the discovery of many facts in the history of nitrogen.

⁷ This reaction, so far as is known, does not proceed beyond a certain limit, probably because cyanogen, CN, itself breaks up into carbon and nitrogen.

⁸ Frémy and Becquerel took dry air, and observed the formation of brown vapours of oxides of nitrogen when sparks are passed.

⁹ If a mixture of one volume of nitrogen and fourteen volumes of hydrogen be burnt, water and a considerable quantity of nitric acid are formed. It may be partly due to this that a certain quantity of nitric acid is produced in the slow oxidation of nitrogenous substances in an excess of air. This is especially facilitated by the presence of an alkali, with which the nitric acid formed can combine. If a galvanic current be passed through water containing the nitrogen and oxygen of the air in solution, then the hydrogen and oxygen set free combine with the nitrogen, forming ammonia and nitric acid.

When copper is oxidised at the expense of the air at the ordinary temperature in the presence of ammonia, oxygen is absorbed, not only for combination with the copper, but also for the formation of nitric acid.

The combination of nitrogen with oxygen, even, for example, by the action of electric sparks, is not accompanied by an explosion or rapid combination, as in the action of a spark on a mixture of oxygen and hydrogen. This is explained by the fact that heat is not evolved in the combination of nitrogen with oxygen, but is absorbed—an expenditure of energy is required, there being no evolution of energy. In other words, the combination of hydrogen with oxygen is an exothermal reaction, and the combination of nitrogen with oxygen an endothermal reaction.

A condition particularly favourable to the oxidation of nitrogen is the explosion of detonating gas and air if the former be *in excess*. If a mixture of two volumes of detonating gas and one volume of air be exploded, one-tenth of the air is converted

form nitric acid,¹⁰ NHO_3 . The presence of the latter is easily recognised, not only from its reddening of litmus paper, but also from its acting as a powerful oxidiser, even of mercury. Conditions similar to these occur in nature, during a thunderstorm or in other electric discharges which take place in the atmosphere; whence it may be taken for granted that air and rain-water always contain a certain amount of nitric and nitrous acids.¹¹ Besides which, Crookes (1892) showed that under certain circumstances, and when electricity of high potential^{11a} passes through the air, the combination of nitrogen with oxygen is accompanied by the formation of a true flame. This was also observed previously during the passage of electric discharges through the air.

Further observations showed that under the influence of electric discharges,¹² silent as well as with sparks, nitrogen is able to enter into

into nitric acid, and consequently after the explosion has taken place there remain only nine-tenths of the volume of air originally taken. If a larger proportion of air be taken—for instance, four volumes to two of detonating gas—then the temperature of the explosion is lowered, the volume of air taken remains unchanged, and no nitric acid is formed. This gives a rule to be observed in making use of the eudiometer—namely, that to diminish the force of the explosion not less than an equal volume of air should be added to the explosive mixture. On the other hand a large excess must not be taken, as no explosion would then ensue (see Chapter III., note 34). Probably, in the future, means will be found for obtaining compounds of nitrogen on a large industrial scale by the aid of electric discharges, and by making use of the inexhaustible mass of nitrogen in the atmosphere.

¹⁰ In reality, nitric oxide, NO , is first formed, but with oxygen and water it gives (brown fumes) nitrogen peroxide, which, as we shall afterwards learn, in the presence of water and oxygen gives nitric acid.

¹¹ The nitric acid contained in soil, river water (Chapter I., note 2), wells, &c., proceeds (like carbonic anhydride) from the oxidation of organic compounds which have fallen into the water, soil, &c.

^{11a} Crookes employed a current of 15 ampères at 65 volts, and passed it through an induction coil with 330 vibrations per second, and obtained a flame between the poles placed at a distance of 46 mm., which after the appearance of the arc and flame could be increased to 200 mm. A platinum wire was fused in the flame of the burning nitrogen.

¹² This property of nitrogen, which under normal conditions is inactive, leads to the idea that, under the influence of an electric discharge, gaseous nitrogen changes in its properties, if not permanently like oxygen (electrolysed oxygen or ozone does not react on nitrogen, according to Berthelot), it may be temporarily at the moment of the action of the discharge, just as some substances under the action of heat are permanently affected (that is, when once changed remain so—for instance, white phosphorus passes into red, &c.), whilst others are only temporarily altered (the dissociation of S_6 into S_2 or of sal-ammoniac into ammonia and hydrochloric acid). Such a proposition is favoured by the fact that nitrogen gives two kinds of spectra, with which we shall afterwards become acquainted. It may be that the molecules of gaseous nitrogen, N_2 , then give less complex molecules, N , containing one atom, or that the bond between the atoms in the molecules is weakened. Probably under a silent discharge the molecules of oxygen, O_2 , are partly decomposed and the individual atoms O combine with O_2 , forming ozone O_3 .

many reactions with hydrogen and with many hydrocarbons, although these reactions cannot be effected by exposure to a red heat. Thus, for instance, a series of electric sparks passed through a mixture of nitrogen and hydrogen causes these gases to combine and **form ammonia**¹³ or nitrogen hydride, NH_3 , composed of one volume of nitrogen and three volumes of hydrogen. This combination is limited to the formation of 6 per cent. of ammonia, because ammonia is decomposed, although not entirely ($\frac{2}{100}$), by electric sparks. This signifies that, under the influence of an electric discharge, the reaction, $\text{NH}_3 = \text{N} + 3\text{H}$, is reversible; consequently it is a dissociation, and in it a state of equilibrium is arrived at. The equilibrium may be destroyed by the addition of gaseous hydrochloric acid, HCl , because with ammonia this forms a solid saline compound, sal-ammoniac, NH_4Cl , which (being formed from a gaseous mixture of 3H , N , and HCl) fixes the ammonia. The remaining mass of nitrogen and hydrogen, under the action of the sparks, again forms ammonia, and in this manner *solid sal-ammoniac is obtained to the end by the action of a series of electric sparks on a mixture of gaseous nitrogen, hydrogen, and hydrogen chloride*. This is also, like the production of nitric acid,¹⁴ an instance of the synthesis of nitrogenous compounds from gaseous nitrogen. Berthelot (1876) showed that, under the action of a silent discharge, many non-nitrogenous organic substances (benzene, C_6H_6 , cellulose in the form of paper, gum, $\text{C}_6\text{H}_{10}\text{O}_5$, &c.) absorb nitrogen and form complex nitrogenous compounds, which are capable, like albuminous substances, of evolving their nitrogen as ammonia when heated with alkalis.¹⁵

¹³ This reaction, discovered by Chabrié and investigated by Thénard, was only rightly understood when Deville applied the principles of dissociation to it.

¹⁴ The action of nitrogen on acetylene (Berthelot) resembles this reaction. A mixture of these gases under the influence of a silent discharge gives hydrocyanic acid, $\text{C}_2\text{H}_2 + \text{N}_2 = 2\text{CNH}$. This reaction cannot proceed beyond a certain limit because it is reversible.

¹⁵ Berthelot successfully employed electricity of even feeble potential in these experiments, which fact led him to think that in nature, where the action of electricity takes place very frequently, a part of the complex nitrogenous substances may be formed in this way from the gaseous nitrogen of the air.

As the nitrogenous substances of organisms play a very important part in them (organic life cannot exist without them), and as the nitrogenous substances introduced into the soil are capable of invigorating its crops (of course in the presence of the other nourishing principles required by plants), the question of the means of converting the atmospheric nitrogen into the nitrogenous compounds of the soil, or into **assimilable nitrogen** capable of being absorbed by plants and of forming complex (albuminous) substances in them, is one of great theoretical and practical interest.

One thousand tons of farmyard manure do not generally contain more than four tons of nitrogen in the form of complex nitrogenous substances, and this amount of nitrogen is contained in twenty tons of ammonium sulphate, so that the effect of a large mass of farmyard manure may, as regards the introduction of nitrogen, be produced by small quantities of artificial nitrogenous fertilisers (see note 15a).

By such indirect methods does the gaseous nitrogen of the atmosphere yield its primary compounds, in which form it enters into plants, and is elaborated in them into complex albuminous substances.^{15a} But, starting from a given compound of nitrogen with hydrogen or oxygen, we may, without the aid of organisms, obtain, as will afterwards be partially indicated, most varied and complex nitrogenous substances, which cannot by any means be formed directly from gaseous nitrogen. In this we see an example, not only of the difference between an element in the free state and an intrinsic element (as a simple body nitrogen is an indifferent gas, but as an element it forms many very active compounds and determines their individual peculiarities; see following chapter), but also of those circuitous or *indirect methods* by which substances are formed in nature. The discovery, prognostication, and, in general, the study of such indirect methods of the preparation and formation of substances form one of the essential problems of chemistry. From the fact that A does not act at all on B, it must not be concluded that a compound AB is not to be formed. The substances A and B contain elementary atoms which occur in AB, but their state or the nature of their motion may not be at all that which is required for the formation of AB, and in this substance the chemical state of the elements may be as different as the states of the atoms of oxygen in ozone and in water. Thus free nitrogen is inactive; but in its compounds it very easily enters into changes and is distinguished by great activity. An acquaintance with the compounds of nitrogen confirms this. But, before entering on this subject (Chap. VI.), let us consider air as a mass containing free nitrogen, and as the medium in which the majority of natural phenomena take place.

Judging from what has been already stated, it will be evident that **atmospheric air**¹⁶ consists of a mixture of several gases and vapours.

^{15a} Although the numerous, and as far as possible accurate and varied researches made in the physiology of plants have proved that the higher forms of plants are not capable of directly absorbing the nitrogen of the atmosphere and converting it into complex albuminous substances, still it has been long and repeatedly observed that the amount of nitrogenous substances in the soil is increased by the cultivation of plants of the bean (leguminous) family, such as the pea, acacia, &c. A closer study of these plants has shown (Hellriegel) that this is connected with the formation of peculiar nodular swellings in their roots caused by the growth of peculiar micro-organisms (bacteria) which live in the soil with the roots, and are capable of absorbing nitrogen from the air, i.e., of converting it into assimilated nitrogen. This branch of plant physiology, which forms another proof of the important part played by micro-organisms in nature, cannot be discussed in this work, but it should be mentioned, since it is of great theoretical and practical interest.

¹⁶ Under the name of atmospheric air the chemist and physicist understand ordinary air containing nitrogen and oxygen, argon, and similar elementary gases, not absorbed

Some of them are met with in it in nearly constant proportions, whilst others, on the contrary, are very variable in their amount. The chief component parts of air, placed in the order of their relative amounts, are the following : nitrogen, oxygen, aqueous vapour, carbonic anhydride, argon, krypton, xenon, neon, nitric acid, salts of ammonia, hydrogen, helium, oxides of nitrogen, and also ozone, hydrogen peroxide, and complex organic nitrogenous substances. Besides these, air generally contains water, as spray, drops, and snow, and particles of solids, perhaps of cosmic origin in certain instances, but in the majority of cases proceeding from the mechanical translation of solid particles from one locality to another by the wind. These small solid and liquid particles (having a large surface in proportion to their weight) are suspended in air just as solid matter is suspended in turbid water : they often settle on the surface of the earth, but the air is never entirely free from them because they are never in a state of complete rest. Then, again, as everyone knows by experience, air not infrequently contains incidental traces of various substances. These incidental substances sometimes act injuriously and sometimes act as carriers of infectious diseases.

In the air of the various countries of the earth, at different latitudes and at different altitudes above its surface, on the ocean or on the dry land—in a word, in the air of the most diverse localities of the earth—the oxygen and nitrogen are found everywhere to be in a constant ratio, and are accompanied by small amounts of argon, krypton, and other gases exhibiting an inactivity similar to that of nitrogen (see later portion of this chapter). This is, moreover, self-evident from the fact that the air is constantly diffusing (intermixing by virtue of the internal motion of the gaseous particles), and is also put into motion and mixed by the

(like H_2O and CO_2) by sulphuric acid or alkalies at the ordinary temperature, although these latter component parts of air have a very important influence on the living matter of the earth's surface. That air is so represented in science is based on the fact that the elementary components are met with in air in a constant quantity, whilst the H_2O and CO_2 are variable. The solid impurities may be separated from air required for chemical or physical research by simple filtration through a long layer of cotton-wool placed in a tube. Organic impurities are removed by passing the air through a solution of potassium permanganate. The carbonic anhydride contained in air is absorbed by alkalies—best of all, soda-lime, which in a dry state in porous lumps absorbs it with exceeding rapidity and completeness. Aqueous vapour is removed by passing the air over calcium chloride, strong sulphuric acid, or phosphoric anhydride. Air thus purified is accepted as containing only nitrogen and oxygen, argon, &c., although in reality it still contains a certain quantity of hydrogen and hydrocarbons, from which it may be purified by passing over copper oxide heated to redness. The copper oxide then oxidises the hydrogen and hydrocarbons—it burns them, forming water and carbonic anhydride, which may be removed as above described. When it is said that, in the determination of the density of gases, the weight of air is taken as unity, it is understood to be air purified in this manner.

wind, so that it becomes equalised in its composition over the entire surface of the earth. In those localities where the air is subject to change, and is in a more or less enclosed space, or, at any rate, in an unventilated space, it may alter very considerably in its composition. For this reason the air in dwellings, cellars, and wells, in which there are substances absorbing oxygen, contains less of this gas, whilst the air on the surface of standing water, which abounds in the lower orders of plant life evolving oxygen, contains an excess of this gas.¹⁷ The constant composition of air—over the whole surface of the earth—has been proved by a number of most careful researches.¹⁸

¹⁷ The air held in the fissures of glaciers contains only 10 per cent. by volume of oxygen. This is owing to the fact that oxygen is much more soluble than nitrogen in snow-water and snow at a low temperature.

¹⁸ The analysis of air by weight conducted by Dumas and Boussingault in Paris, which they repeated many times between April 27 and September 22, 1841, under various conditions of weather, showed that the amount by weight of oxygen only varies between 22·89 per cent. and 23·08 per cent., the average amount being 23·07 per cent. Brunner in Berlin, Bravais at Faulhorn in the Bernese Alps, at a height of two kilometres above the level of the sea, Marignac at Geneva, Lewy at Copenhagen, and Stas at Brussels, have analysed the air by the same methods, and found that its variation in composition does not exceed the limits determined for Paris. The most recent determinations (with an accuracy of $\pm 0\cdot05$ per cent.) confirm the conclusion that the composition of pure air is comparatively constant.

There are some grounds (which will be mentioned shortly) for considering that the composition of the air at great altitudes is slightly different from that at attainable heights—namely, that it is richer in the lighter nitrogen—and several fragmentary observations made at Munich (Jolly, 1880) gave reason for thinking that in the upward currents (that is, in the regions of minimum barometric pressure or at the centres of meteorological cyclones) the air is richer in oxygen than in the descending currents of air (in the regions of anticyclones or of barometric maxima); but more carefully conducted observations showed this supposition to be incorrect. Improved methods for the analysis of air have shown that certain slight variations in its composition do actually occur; but in the first place these depend on incidental local influences (on the passage of the air over mountains and large surfaces of water, regions of forest and herbage, and the like), and are also limited to quantities scarcely distinguishable from possible errors in the analyses. The researches made by Kreisler in Germany (1885) are particularly convincing.

The considerations which lead to the supposition that the atmosphere at great altitudes contains less oxygen than that at the surface of the earth are based on the law of partial pressures (Chap. I.). According to this law, the equilibrium of the oxygen in the strata of the atmosphere is not dependent on the equilibrium of the nitrogen, and the variations in the densities of the two gases with the height are determined by the pressures of separate gases. Details of the calculations and considerations involved therein are contained in my work: *On Barometric Levellings*, 1876, p. 48. On the basis of the law of partial pressures and of hypsometrical formulæ, expressing the laws of the variation of pressures at different altitudes, the conclusion may be deduced that in the upper strata of the atmosphere the proportion of nitrogen with respect to oxygen increases, but the increase will not exceed a fraction per cent., even at altitudes of four and a half to six miles, the greatest height within the reach of man either by climbing mountains or by means of balloons. This conclusion is confirmed by the analysis of air collected by Welch in England during his aëronautic ascents.

The analysis of air is effected by converting the oxygen into a non-gaseous compound, so as to separate it from the air. The original volume of the air is first measured, and then the volume of the remaining nitrogen. The quantity of oxygen is calculated either from the difference between these volumes or by the weight of the oxygen compound formed. All the volumetric measurements have to be corrected for pressure, temperature, and moisture (Chapters I. and II.) The medium employed for converting the oxygen into a non-gaseous substance should enable it to be completely taken away from the nitrogen without evolving any gaseous substance. Thus, for instance,¹⁹ a mixture of pyrogallol, $C_6H_6O_3$, with a solution of a caustic alkali absorbs oxygen with great ease at the ordinary temperature (the solution turns black), but it is unsuited for accurate analysis, because it requires an aqueous solution of an alkali, and it alters the composition of the air by acting on it as a solvent. However, for approximate determinations this simple method gives results which are entirely satisfactory.²⁰

The determinations in a eudiometer (Chapter III.) give more exact results, if all the necessary corrections for changes of pressure, temperature, and moisture are taken into account. This determination is carried out essentially as follows:—A certain amount of air is introduced into the eudiometer, and its volume is determined. About an equal volume of dry hydrogen is then passed into the eudiometer, and the volume again determined. The mixture is then exploded by a spark from a Leyden jar or Ruhmkorff coil. The remaining volume of the gaseous mixture is again measured: it will be less than the second of the previously measured volumes. Of three volumes which have disappeared, one belonged to the oxygen and two to the hydrogen; consequently one-third of the loss of volume indicates the amount of oxygen contained in the air.²¹

¹⁹ The complete absorption of the oxygen may be attained by introducing moist phosphorus into a definite volume of air: this is shown by the fact that the phosphorus becomes non-luminous in the dark. The amount of oxygen may be determined by measuring the volume of nitrogen remaining. This method, however, cannot give accurate results, owing to a portion of the air being dissolved in the water, to the combination of some of the nitrogen with oxygen, and to the necessity for introducing and withdrawing the phosphorus, which cannot be accomplished without admitting bubbles of air.

²⁰ For rapid and approximate analyses (technical and hygienic), such a mixture is very suitable for determining the amount of oxygen in mixtures of gases from which the substances absorbed by alkalies have first been removed. According to some observers, this mixture evolves a certain (small) quantity of carbonic oxide after absorbing oxygen.

²¹ Details of eudiometrical analysis must, as was pointed out in Chap. III., note 32, be looked for in works on analytical chemistry. The same remark applies to the other analytical methods mentioned in this work. They are only described for the purpose of showing the diversity of the methods of chemical research.

The most exact method for the analysis of air, and one which is accompanied by the smallest error, consists in the direct weighing, as far as is possible, of the oxygen, nitrogen, water, and carbonic anhydride contained in it. For this purpose the air is first passed through a weighed apparatus (which will be considered presently) for retaining the moisture and carbonic anhydride, and is then led through a tube which contains shavings of metallic copper and has been previously

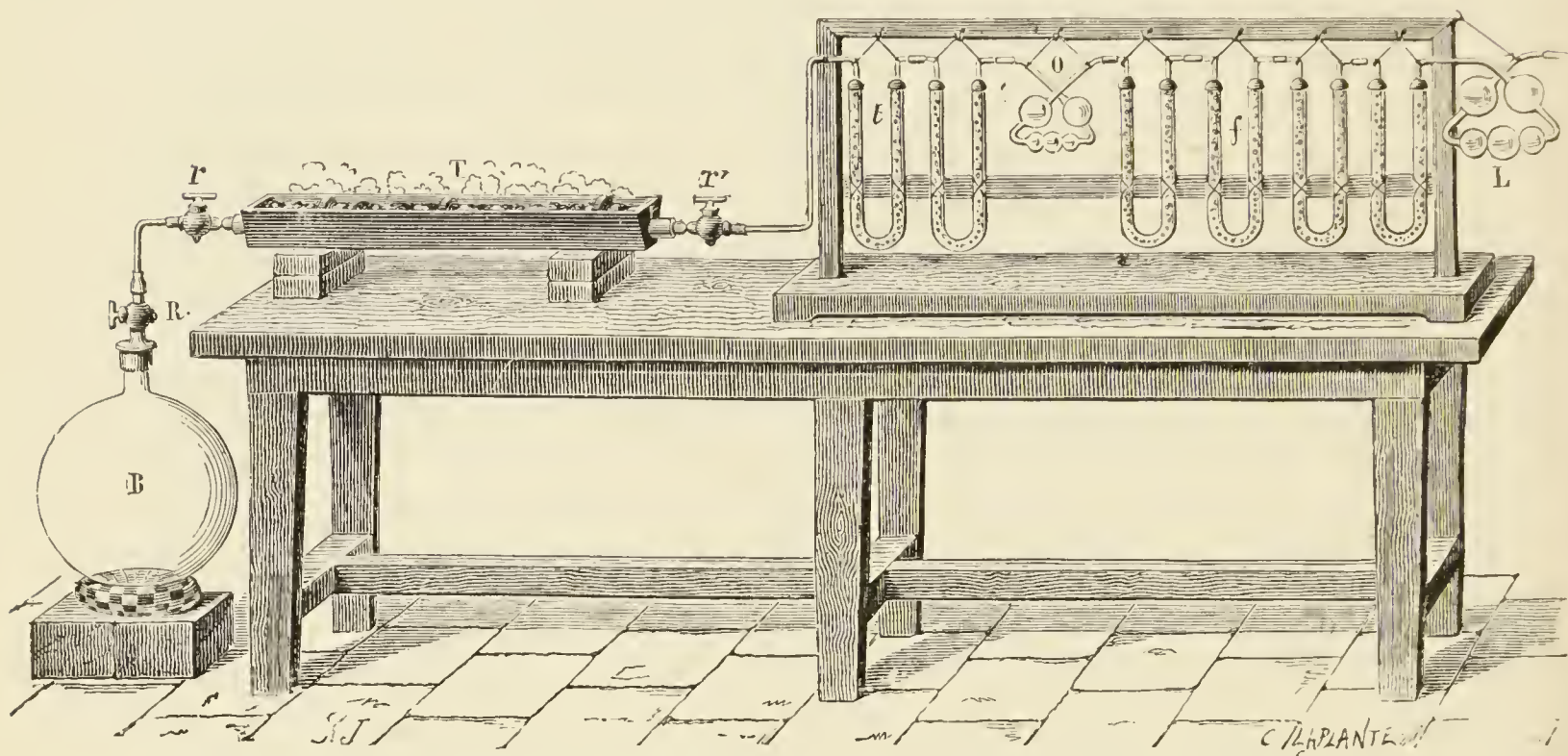


FIG. 42.—Dumas and Boussingault's apparatus for the analysis of air by weight. The globe B contains 10–15 litres. The air is first pumped out of it, and it is weighed empty. The tube T connected with it is filled with copper, and is weighed empty of air. It is heated in a charcoal furnace. When the copper has become red-hot, the stopcock *r* (near R) is slightly opened, and the air passes through the vessels L, containing a solution of potash, and *f*, containing solutions and pieces of caustic potash, which remove the carbonic anhydride from the air, and then through *o* and *t*, containing sulphuric acid (which has been previously boiled to expel dissolved air) and pumice-stone, which removes the moisture from the air. The pure air then gives up its oxygen to the copper in T. When the air passes into T the stopcock R of the globe B is opened, and it becomes filled with nitrogen. When the air ceases to flow in, the stopcocks are closed, and the globe B and tube T weighed. The nitrogen is then pumped out of the tube and it is weighed again. The increase in weight of the tube shows the amount of oxygen, and the difference between the second and third weighings of the tube, with the increase in weight of the globe, gives the weight of the nitrogen.

weighed, the remaining nitrogen being afterwards collected and weighed. A long layer of such copper heated to redness absorbs all the oxygen from the air, but does not act on the nitrogen. The nitrogen is determined in a weighed and exhausted globe by ascertaining the increase in weight, while the amount by weight of oxygen is shown by the increase in weight of the tube with the copper.

Air free from moisture and carbonic anhydride ²² contains 23.17 to

²² De Saussure observed that air freed from carbonic anhydride and submitted to the action of a series of electric sparks again shows the presence of a small quantity of carbonic anhydride, and Boussingault found that air free from moisture, after being passed over red-hot copper oxide, invariably appears to contain a small quantity of water. These observations lead to the assumption that air always contains a certain quantity of

23.03 per cent.²³ by weight of oxygen; the mean amount of oxygen will therefore be 23.12 ± 0.05 per cent. by weight, and 20.91 by volume.²⁴

The possibility of the composition of air being altered by the mere action of a solvent very clearly shows that the component parts of air are in a state of mixture, in which any gases may occur; they do not in this case form a definite compound, although the composition of the

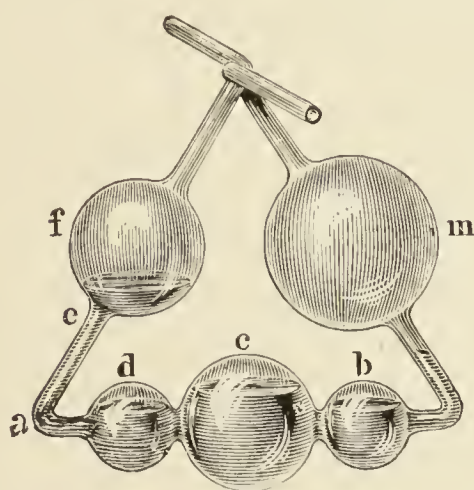


FIG. 43.—Apparatus for the absorption and washing of gases, known as Liebig's bulbs. The gas enters *m*, presses on the absorptive liquid, and passes from *m* into *b*, *c*, *d*, and *e* consecutively, and escapes through *f*.

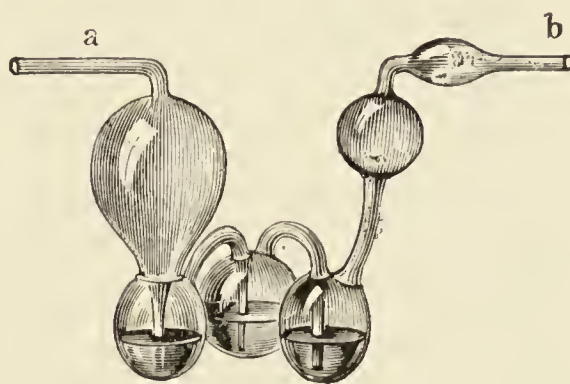


FIG. 44.—Geissler's potash bulbs. The gas enters at *a*, passes through a solution of potash in the lower bulbs, where the carbonic anhydride is absorbed, and then escapes from *b*. The lower bulbs are arranged in a triangle, so that the apparatus can stand without support.

atmosphere does appear constant under ordinary conditions. The fact that its composition varies under different conditions confirms the truth of this conclusion, and therefore the constancy of the composition of air must not be considered as in any way dependent on the nature of the gases entering into its composition, but only as proceeding from cosmic phenomena co-operating towards this constancy. It must be admitted, therefore, that over the entire surface of the earth,²⁵ the

gaseous hydrocarbons, like marsh gas, which, as we shall afterwards learn, is evolved from the earth, marshes, &c. Its amount, however, does not exceed a few hundredths per cent. A. Gauthier's careful researches (1898–1901) proved this beyond doubt, as will be explained presently; but it appeared that the amount of hydrocarbons is variable and in some cases zero, while hydrogen is always present to the amount of about 0.02 per cent. (see note 29).

²³ The analyses of air are accompanied by errors, variations of composition of a few hundredths per cent. being found; the average normal composition of air is therefore only correct to the first decimal place.

²⁴ These figures express the mean composition of pure air as given by the most accurate determinations; they are accurate within ± 0.05 per cent.

²⁵ In Chap. III., note 4, an approximate calculation is made for the determination of the balance of oxygen in the entire atmosphere; it may therefore be supposed that the composition of air will vary from time to time, the relation between vegetation and the oxygen-absorbing processes changing; but as the atmosphere of the earth can hardly have a definite limit and we have already seen (Chap. IV., note 33) that there are observations confirming this, it follows that variations in the composition of our atmosphere are distributed throughout celestial space, and therefore it must be supposed that any variation in the composition of the air in the course of ages can only take place

processes evolving oxygen, and chiefly the processes of the respiration of plants, have an influence equal and opposite to that exerted by those processes which absorb oxygen.

Air always contains more or less moisture ²⁶ and **carbonic anhydride**,

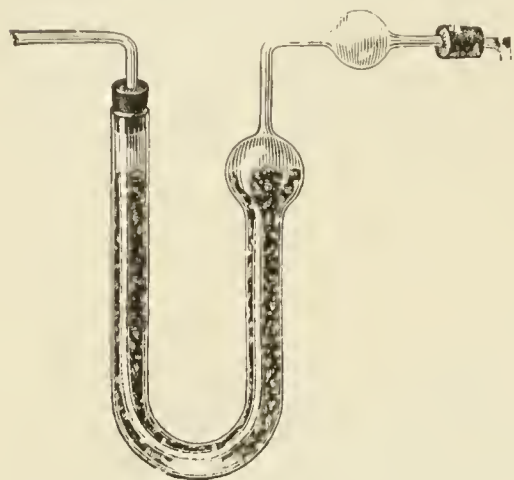


FIG. 45.—Tube for the absorption of carbonic acid. A plug of cotton-wool is placed in the bulb to prevent the powder of soda-lime being carried off by the gas. The tube contains soda-lime and chloride of calcium.

which are produced by the respiration of animals and the combustion of carbon and carboniferous compounds. The latter gas shows the properties of an acid anhydride. In order to determine the amount of carbonic anhydride in air, substances which absorb it—namely, alkalies—are employed, either in solution or in the solid state. A solution of caustic potash, KHO, is poured into light glass vessels, through which the air is passed, and the amount of carbonic anhydride is determined by the increase in weight of the vessel. But it is best to take a porous alkaline solid such as soda-

lime.²⁷ With a slow current of air, a layer of soda-lime 20 cm. in length is sufficient to completely deprive 1 cubic metre of air of the carbonic anhydride it contains. A series of tubes containing calcium

exceedingly slowly, and in a manner imperceptible by direct experiment. The composition of the atmosphere must, however, have undergone considerable changes during the course of the geological history of the earth (i.e., during millions of years). This is particularly true concerning the amount of carbonic anhydride, as it has been largely absorbed by the earth's crust and soil in the sedimentary formations composed of salts of carbonic acid (for instance, limestones, CaCO_3) and in coal. The temperature of the earth's surface must depend greatly upon the amount of CO_2 in the air, because this affects the diathermancy of the atmosphere (just as the glass of a hothouse hinders it from cooling and collects the heat of the sun's rays). The undoubted difference of climate in different geological periods is now accounted for in this manner. Thus the climate of Central Europe was colder during the glacial period and much warmer during the mammoth period. The researches of Brown and Escombe (1902), strange to say, showed that dicotyledons strike not better but far worse when the amount of carbonic anhydride in the air increases (how is it with gymnosperms?).

²⁶ The amount of moisture contained in the air is considered in greater detail in the study of physics and meteorology, and the subject has been mentioned above in Chapter I., note 1, where the methods of absorbing moisture from gases were pointed out.

²⁷ Soda-lime is prepared in the following manner:—Unslaked lime is finely powdered and mixed with a slightly warmed and very strong solution of caustic soda. The mixing should be done in an iron dish, and the materials should be well stirred together until the lime begins to slake. When the mass becomes hot, it boils, swells up, and solidifies, forming a porous mass very rich in alkali and capable of rapidly absorbing carbonic anhydride. A lump of caustic soda or potash presents a much smaller surface for absorption, and therefore acts much less rapidly. It is necessary to place an apparatus for absorbing water after the apparatus for absorbing the carbonic anhydride, because the alkali in absorbing the latter gives off water.

chloride for absorbing the moisture²⁸ is placed before the apparatus for the absorption of the carbonic anhydride, and a measured mass of air is passed through the whole apparatus by means of an aspirator. In this manner the determination of the moisture is combined with the absorption of the carbonic anhydride. The arrangement shown in fig. 42 is such a combination.

The amount of carbonic anhydride²⁹ in free air is incomparably more constant than the amount of moisture. The average amount in 100 volumes of dry air is approximately 0.03 volume—that is, 10,000 volumes of air contain about three volumes of carbonic anhydride, most frequently about 2.95 volumes. As the specific gravity of

²⁸ It is evident that the calcium chloride employed for absorbing the water should be free from lime or other alkalies in order that it may not retain carbonic anhydride. Such calcium chloride may be prepared in the following manner: A perfectly neutral solution of calcium chloride is prepared from lime and hydrochloric acid; it is then carefully evaporated, first on a water-bath and then on a sand-bath. When the solution attains a certain strength a scum is formed, which solidifies at the surface. This scum is collected, and will be found to be free from caustic alkalies. It is necessary in any case to test it before use, as otherwise a large error may be introduced into the results owing to the presence of free alkali (lime). It is best to pass carbonic anhydride through the tube containing the calcium chloride for some time before the experiment in order to saturate any free alkali that may remain from the decomposition of a portion of the calcium chloride by water, $\text{CaCl}_2 + 2\text{H}_2\text{O} = \text{CaOH}_2\text{O} + 2\text{HCl}$.

²⁹ Recourse is had to special methods when the determination only takes note of the carbonic anhydride of the air. For instance, it is absorbed by an alkali which does not contain carbonates (by a solution of baryta or caustic soda mixed with baryta), and then the carbonic anhydride is expelled by an excess of an acid, and its amount determined by the volume given off. A rapid method of determining CO_2 (for hygienic purposes) is given by the fall of pressure produced by the introduction of an alkali (the air having been either brought to dryness or saturated with moisture). Dr. Schidloffsky's apparatus is based upon this principle. The question as to the amount of carbonic anhydride present in the air has been submitted to many voluminous and exact researches, especially those of Reiset, Schloesing, Müntz, and Aubin, who showed that the amount is not subject to such variations as at first stated. The existing data concerning the amount of CO_2 in the air have been supplemented (1902) by observations made by A. Levy and Henriet, who found that, after leaving air in contact with an alkali for several days so that all the CO_2 was absorbed, they obtained a further quantity of CO_2 which varied in different cases, but sometimes approached the normal amount. A commission deputed by the Paris Academy of Sciences to verify this unexpected discovery convinced themselves of its reality, and in one experiment (July 27, 1902) obtained a further 0.0216 per cent. of CO_2 (by volume) after having absorbed all the original CO_2 (about 0.03 per cent. vol.) with baryta. Henriet showed that this second portion of CO_2 originates in the subsequent oxidation of an organic substance which is present in the air and occurs in solution in the water obtained by the condensation of its moisture, and he supposes this body to be an amide of formic acid. These observations were made in Paris and also at Mont Sourie, near Paris. They are, however, too recent to allow of their being regarded as perfectly trustworthy; and what is, in my opinion, still more important, there is no proof either that the air of all localities would exhibit this peculiarity or that it is not a consequence of urban conditions, and hence due to a change produced in the air by the crowded life of cities. Further, it is not known whether it would be observable in air containing such oxidising agents as ozone, peroxide of hydrogen, and oxides of nitrogen. But in any case it is a matter of great interest.

carbonic anhydride referred to air is 1.52, it follows that 100 parts by weight of air contain about 0.045 part by weight of carbonic anhydride. This quantity varies according to the time of year (more in winter), the altitude above the level of the sea (less at high altitudes), the proximity to forests and fields (less) or cities (greater), &c. But the variation is small and rarely exceeds the limits of $2\frac{1}{2}$ to 4 ten-thousandths by volume.³⁰ As there are many natural local influences which either increase the amount of carbonic anhydride in the air (respiration, combustion, decomposition, volcanic eruptions, &c.), or diminish it (absorption by plants and water), the reason of the great constancy in the amount of this gas in the air must be looked for, in the first place, in the fact that the wind mixes the air of various localities together, and, in the second place, in the fact that the waters of the ocean, holding carbonic acid in solution,³¹ form an immense reservoir for regulating the amount of this gas in the atmosphere. Immediately the partial pressure of the carbonic anhydride in the air decreases, the water evolves more of the gas, whilst when its partial pressure increases, some of it is absorbed in this, as in so many other instances.³² Hence nature supplies the conditions for a state of equilibrium.

³⁰ In enclosed spaces, in dwellings, cellars, wells, caves, and mines, where the renewal of air is impeded, the case is different. Under these circumstances large quantities of carbonic anhydride may accumulate. In cities, where many conditions (respiration, decomposition, combustion) for the evolution of carbonic anhydride exist, its amount is greater than in free air; yet even in still weather the difference does not often exceed one ten-thousandth (that is, rarely attains 4 instead of 2.9 vols. in 10,000 vols. of air).

³¹ In the sea, as well as in fresh water, carbonic acid occurs in two forms, being both directly dissolved in the water, and combined with lime as calcium bicarbonate (hard waters sometimes contain very much carbonic acid in this form). The pressure of the carbonic anhydride in the first form varies with the temperature, and its amount with the partial pressure; and the same is the case with that existing in the form of acid salts, for direct experiments show a similar dependence here, although the quantitative relations are different in the two cases.

³² In studying the phenomena of nature the conclusion is arrived at that the universally reigning state of mobile equilibrium forms the chief reason for that harmonious order which impresses all observers. It not unfrequently happens that we do not see the causes regulating the order and harmony; in the particular instance of carbonic anhydride, it is a striking circumstance that in the first instance a search was made for an harmonious and strict uniformity, and in incidental (insufficiently accurate and fragmentary) observations, conditions were even found for concluding it to be absent. When, later, the existence of this uniformity was confirmed, the causes regulating such order were also discovered. The researches of Schloesing were of this character. Deville's idea of the dissociation of the acid carbonates of sea-water is suggested in them. In many other cases also a correct interpretation can only follow from a detailed investigation. It is the function of science to discover the existence of a general reign of order in nature and to find the causes governing this order. And this refers in equal measure to the relations of man (social and political) and to the entire universe as a whole, and also to the world of material inanimate substances, in which natural science is gradually discovering an equilibrated order of things wherever it pursues the requisite research.

Besides nitrogen, oxygen, moisture, and carbonic acid, all the other substances occurring in air are found in infinitesimally small proportions by weight, and therefore the **weight of any volume of air** (at a given temperature and pressure) depends mainly on the above-named components. The weight of a litre of pure air (that of a litre of water at 4° and 760 mm. being 1,000 grams), free from dust, moisture, and carbonic anhydride, at 0° and 760 mm., has been determined as follows : ³³

	Average weight of litre			Under acceleration of		
	gramme			gravity, $g =$ metres		
Regnault (1847)	.	.	1·29347	.	.	9·8100
Jolly (1880)	.	.	1·29316	.	.	9·8073
Leduc (1892)	.	.	1·29330	.	.	9·8100
Rayleigh (1893)	.	.	1·29362	.	.	9·8126

The last column gives the acceleration due to gravity in metres. It has an effect upon the value of the barometric column, for 760 mm. of mercury presents a greater pressure, the greater the acceleration due to gravity. The average weight of a litre of pure air under an acceleration g is :

$$e_0 = g \times 0.131844 \text{ gram.}$$

Defarges gives an average of $g = 9.80665$ ³⁴ for latitude 45° and therefore $e_0 = 1.2929$ gram (the density being about 14.4 with respect to hydrogen). The weight of air containing 0.03 per cent. by volume of CO₂ will be greater by 0.0006 gram. Hence if at a given locality the observed barometric pressure reduced to 0° be P mm., the vapour pressure of water p mm., the temperature t (according to the Centigrade thermometer, and corrected to the hydrogen scale) and the acceleration of gravity g metres, then the weight of a litre of air (with an error not greater than about 0.0002 gram) will be :

$$e = \frac{g}{9.80665} \times 1.2935 \times \frac{P - 0.38p}{760} \times \frac{273}{273 + t} \text{ gram.}^{35}$$

A knowledge of the exact weight of a litre of air is of great

³³ See 'The Publications of the Weights and Measures Department,' 1894, part i., p. 85.

³⁴ The acceleration of gravity for a given latitude L° and elevation above the sea level, H metres, will then (if the terrestrial globe be assumed to be a regular ellipsoid at the level of the sea, which, strictly speaking, is not the case) be given by :

$$g = \frac{9.80665 (1 - 0.0026 \cos 2L)}{1 + 0.000000196 H}.$$

But the most accurate results are obtained by direct experiment, because the proximity of the sea or mountains, the nature of the geological formations of a given locality, and irregularities in the ellipsoidal form of the earth also affect the value of g .

³⁵ The effect of the local acceleration of gravity on the weight of a litre of air is determined exclusively by the dependence of this weight on the pressure and the

importance in determining the exact weight of objects and weights, where it is necessary to introduce corrections for the weight of air displaced,³⁶ and also in investigating many meteorological phenomena, the movements of the atmosphere being determined chiefly by the different densities of different volumes of air which are at the same level and are moving freely.³⁷

Although **liquid air**, as mentioned in Chapter II., was already known in 1877 (Pictet and Cailletet), it was not until much later, in the nineties, that the means were discovered, thanks to the labours of Olzewsky, Wroblewsky, Dewar, Linde, and others, for obtaining it easily in con-

measurement of this pressure by the barometric column. At first it might appear to be a question of the difference (see 'Mechanics and Physics') which exists between the conceptions of mass and weight, as the latter is determined by the acceleration of gravity, for weight is pressure. But the weights, expressing a definite mass, remain the same, and consequently when a weight is expressed by them (as is customary both in chemistry and in ordinary practice) they vary in the pressure they produce according to the locality in which they are situated. In other words, weights, for instance, the gram, as a matter of fact express units of mass; but they are also measures of weight in the generally accepted sense of the word. This is all only a question of nomenclature and of the conditional expression of conceptions, over which I think it is unnecessary to linger, for science should give clear conceptions and not temporise with words, although unfortunately we cannot express our ideas without them; and if the term 'weight' is frequently used in chemistry in the sense of mass (for instance, the weight of an atom or of a gram), still this does not introduce any inexactitude into the science, particularly as words often have more meanings than one. Thus the word 'mass' expresses the conception of a multitude of substances besides the mechanical notion of the amount of ponderable matter, and the word 'weight' not only signifies the amount of a substance in units of weight, but also the counterpoises themselves. I think it only complicates matters to introduce any changes in words or to invent special ones for every conception.

³⁶ For rapid calculation the weight of a litre of air (in a room) in St. Petersburg may under these conditions (P , t , and p) be obtained by the formula, $e = 1.20671 + 0.0016 [P_1 - 755 + 2.6 (18 - t)]$, where $P_1 = P - 0.38p$. In determining the weight of small and heavy objects (crucibles, &c., in analysis, and in determining the specific gravities of liquids, &c.) **a correction may be introduced for the loss of weight** in the air of the room, by taking the weight of a litre of air displaced as 1.2 gram, and consequently allowing 0.0012 gram for every cubic centimetre. But if gases or, in general, large vessels are weighed, and the weighings require to be accurate, it is necessary to take into account all the data (t , P , and p), because sensitive balances can determine the possible variations of the weight of air, as in the case of a litre of air the weight varies in centigrams, even at a constant temperature, with variations of P and p . Some time ago (1859), I proposed the following method and applied it for this purpose. A large light and closed vessel is taken, and its volume and weight in a vacuum accurately determined and verified from time to time. On weighing it we obtain the weight in air of a given density, and by subtracting this weight from its absolute weight and dividing by its volume we obtain the density of the air.

³⁷ At about the normal pressure and within the limits of 0° and 25° , an increase of pressure of about 3 mm. produces the same variation in the density of air, as a fall in temperature of 1° . It appears to me therefore that an investigation of the variation in the distribution of the densities of air at various periods over the surface of the earth (which may be easily accomplished now with kites and self-registering apparatus) might give most important and instructive meteorological data. The following table, which I have compiled from Glaisher's observations, assuming the temperature at the surface of

siderable quantities, and even for using it for scientific and industrial purposes, for obtaining low temperatures and for concentrating the oxygen (boiling at -181°) from the more volatile nitrogen (boiling at -193°)³⁸ by evaporating the liquid mixture. Linde's apparatus for liquefying air is the most widely known.³⁹ It consists of two pumps B_1 and B_2 , which compress the indrawn air to 15–20 and 200 atmospheres respectively. As the compression of air to such an extent as 200 atmospheres evolves considerable heat, and as the liquefaction of air requires a low temperature, the pumps and compressed air are cooled to a low temperature⁴⁰ (a small amount of water is introduced into the cylinder B_1 for this purpose) by three refrigerators D_1 , D_2 , and G after the preliminary compression to 15–20 atmospheres and after the compression to 200 atmospheres. And as the refrigeration and

the earth to be $+15^{\circ}$, pressure 760 mm., and relative moisture 60 per cent., gives an idea of the variation of the density of the air during fine weather:—

Pressure	t° Centigrade	Moisture	Elevation	Weight of a litre of air
mm.		per cent.	m.	gram
760	+ 15.0	60	0	1.222
700	11.0	64	690	1.141
650	7.6	64	1,300	1.073
600	4.3	63	1,960	1.003
550	+ 1.0	62	2,660	0.931
500	— 2.4	58	3,420	0.857
450	— 5.8	52	4,250	0.781
400	— 9.1	44	5,170	0.703
350	— 12.5	36	6,190	0.624
300	— 15.9	27	7,360	0.542

As a matter of fact, especially in cloudy weather, the distribution of the density with the altitude is often much less regular, owing chiefly to the want of uniformity of the fall of temperature with increase of height.

³⁸ Liquid air floats on water, because its density, owing to the larger amount of nitrogen, is less than that of water; but when much of the nitrogen evaporates and the proportion of oxygen becomes greater it sinks under water, because liquid oxygen is slightly heavier than water at the temperature of liquid air. The colourless liquid air acquires a bluish tint as it becomes richer in oxygen.

³⁹ It may be obtained in different sizes. The large Linde machine which E. L. Nobel supplied to the St. Petersburg Weights and Measures Department requires a motive power of 12-horse power, and according to F. T. Blumbach can, when in good working order, supply 5 litres of liquid air per hour.

⁴⁰ The cooling in the refrigerators (D_1 , D_2 , and G) is carried on by cold water or ice, or, better still, by a mixture of salt and snow (about -20° , according to the method used in the Department of Weights and Measures of St. Petersburg) or by a mixture of snow (pounded ice) and crystals of chloride of calcium, or some other freezing mixture (Chap. I., note 26, and Chap. II., note 27). It must be remembered that in general the liquefaction of air (Chap. II., note 29) cannot take place at a temperature above -150° (the critical temperature of oxygen), and therefore expansion (to 1.5 atmosphere) of compressed (to 200 atmospheres) gas will give more liquid air, the lower the original temperature of the compressed gas (i.e., when under a pressure of 200 atmospheres).

compression of the air cause the moisture in it to precipitate partly as water (which is collected in F)⁴¹ and partly as ice, which might

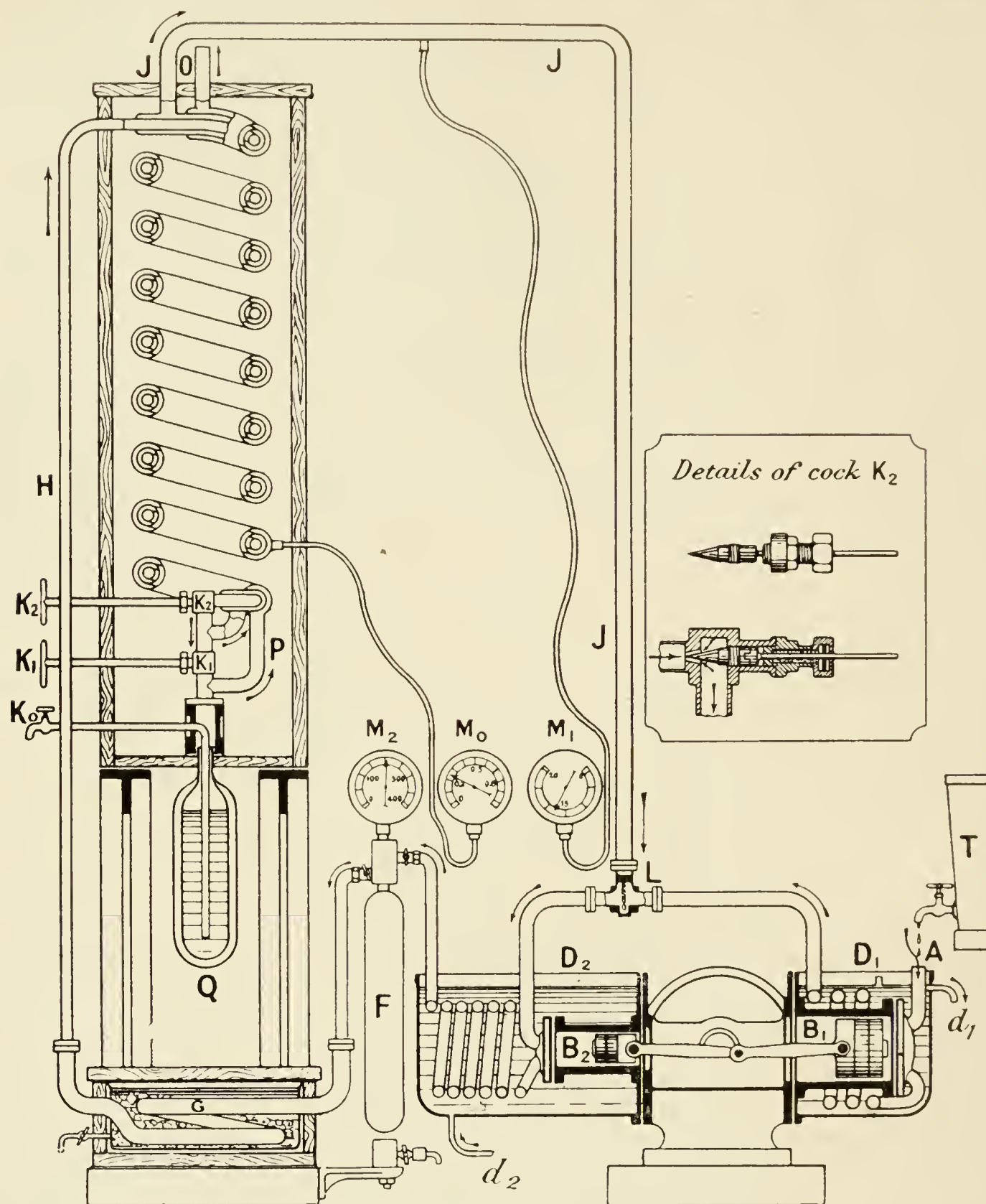


FIG. 46.—Linde's apparatus for the liquefaction of air. A, the entrance for the air (with a small quantity of water from T) into the double-acting pump. B₁, the low-pressure (20 atms.), and B₂, the high-pressure (200 atms.), cylinders. D₂ and D₁, vessels through which runs cold water (d_2-d_1) for cooling the warm compressed air passing to the copper spiral. F, water-separator made of steel. G, steel spiral surrounded by a mixture of ice and salt (-15°). H, the inner tube of a triple copper spiral (the compressed and expanded air take opposite courses) surrounded by wool. K₂, conical cock for the expansion of the compressed air from 200 to 18 atmospheres pressure. J, tube through which the cooled gas returns through the valve L to the piston B₂. K₁, cock for expanding from 18 atms. to the ordinary pressure. The liquid air collects in the Dewar's vessel Q, and that which evaporates escapes from the apparatus through the third exterior spiral P-O. K₀, syphon cock for pouring out the liquid air after closing the aperture O. M₂, M₁, and M₀, manometers for the systems of tubes at pressures of 200, 20, and 1 atm. respectively.

⁴¹ It is evident that the water must be got rid of before letting the compressed air into the refrigerators (which are often spiral in form) where the temperature is below 0° ,

close the pipes conveying the compressed air, it is necessary to have a separator F ⁴² through which the compressed air is made to pass after leaving the pumps. It then travels through a long copper spiral H ,⁴³ situated in three high prism-shaped boxes in which the further refrigeration of the compressed gas takes place. These boxes are lined with bad conductors of heat (wool, down, felt) to prevent the warmth of the external air passing through. Besides which, the internal copper spiral, conveying the compressed air, is surrounded along its entire length by two similar but wider metallic spirals along which the refrigerated air which remains unliquefied is carried back to the pumps or escapes into the room, as will be presently explained.⁴⁴ This facilitates (naturally after the lapse of some time) the further refrigeration of the compressed air, which cannot of course liquefy spontaneously under a pressure of 200 atmospheres and at a temperature of -20° or even -50° (when cooled by a mixture of snow and crystals of calcium chloride), because the critical temperature (absolute boiling-point) of nitrogen lies much lower, namely, at about -146° . To obtain the requisite fall of temperature, the end of the internal copper spiral is furnished with a conical cock, K_2 , by means of which the compressed air is made to expand from a pressure of 200 to 15–20 atmospheres.⁴⁵ And as the increase in volume so produced causes the temperature of the air to fall by about 50° , the air will, on expansion, fall from a temperature t of between -15° and -20° to about -60° . This refrigerated air passes from the expansion box along the annular space surrounding the copper spiral into the pump B_2 , and in so doing cools the air compressed under 200 atmospheres to -50° or -60° , and after this again expands; the

so that the water should not freeze in them and hinder the passage of the compressed air. This must be kept in view in constructing refrigerators of this type.

⁴² The drops of water are collected by a metallic funnel as they enter the separator, and form a stream of water which remains in the separator. As any remaining water and the carbonic anhydride in the air solidify at the temperature of liquid air (about -190°), the liquid air obtained in the apparatus has the appearance of a turbid liquid, which is purified by simply filtering through unsized paper. A double-walled funnel, like the vessels described in Chap. II., note 32, for preserving liquid gases, should be taken for this purpose.

⁴³ In the apparatus at the St. Petersburg Weights and Measures Department it is 25 metres long.

⁴⁴ It is evident that the cold air obtained by expansion travels upwards in the annular space surrounding the inner spiral if the air travels downwards in the internal tube. This facilitates the refrigeration of the air passing through the inner spiral.

⁴⁵ The variation of the pressure in the apparatus is determined by means of pressure gauges. The first, M_2 , indicates about 200 atmospheres and is situated before the entrance for the compressed air into the spiral. The gauge M_1 indicates about 15–20 atmospheres and gives the pressures in the box where the expansion goes on. The third gauge, M_0 , gives the ultimate expansion, about $1\frac{1}{10}$ atmosphere.

temperature falls still further, and so on. In other words, when the apparatus continues working the gas compressed under 200 atmospheres is cooled more and more by expanding to 15–20 atmospheres. If the cock K_1 be now opened sufficiently to allow this refrigerated air to expand once more to a pressure of about one atmosphere,⁴⁶ its rapid expansion will be accompanied by a correspondingly rapid fall of temperature.⁴⁷ Then a portion of the air remains in the form of an exceedingly cold gas and escapes into the atmosphere through a third (external) copper tube which surrounds the whole of the upper portion of the spiral in the box, while the rest of the air passes into a liquid state, having a temperature of about -190° . The stream of liquid air so formed is collected in a double-walled vessel, like that described in Chapter II., note 32. This liquid air can be kept in this state for many days (for even fourteen days if about 2 litres be taken, and there be a perfect vacuum between the walls of the vessel). At first it is chiefly the nitrogen that evaporates, so that in the end a liquid very rich in oxygen is obtained.

As liquid air possesses and preserves (in evaporating) a very low temperature (between -190° and -185° , according to the amount of oxygen it contains), it makes possible many interesting experiments, especially of a physical nature. For instance, when mercury is poured into liquid air it freezes and becomes so cold that it can be hammered and rolled like lead. Alcohol and many other liquids which do not freeze in the most severe frosts are easily converted into solid matter by liquid air. When cooled by liquid air, indiarubber becomes exceedingly brittle, hard, and fragile, and lead sonorous. If an exhausted glass globe be filled with the vapour of mercury (by means of a Sprengel air pump), and any portion of it be cooled by liquid air (by moistening a piece of wadding on a stick with it and then rubbing the exterior of the globe), the mercury is immediately precipitated as a mirror on the spot cooled. If a glass globe be filled with the reddish-brown vapour of bromine (by boiling liquid bromine in the globe and so expelling the air, and then sealing up the globe), and any portion of its surface be cooled by liquid air, the bromine collects so completely about the cold spot in a solid form that the inside of the globe becomes quite colourless.

⁴⁶ The cock K_1 is opened just enough to reduce the pressure to about 1.1 atmosphere. A slight excess of pressure is given to make the cold expanded gas pass into the external annular space surrounding the spiral.

⁴⁷ When the temperature of the compressed air is between 0° and -50° , a fall in pressure of 1 atmosphere only produces a cooling effect of 0.2 – 0.3° ; but when the gas has been cooled to -190° or -200° , the same fall of pressure (1 atmosphere) lowers the temperature of the air by almost 2° , that is, the colder the air is, the more it is chilled by the same fall of pressure.

Those physical properties of the metals which vary to any considerable extent with the temperature are greatly affected by liquid air.⁴⁸ Thus the resistance offered by metals to an electric current, although not completely destroyed, is very greatly diminished in liquid air, and becomes infinitely small at about -273° (absolute zero)⁴⁹ for all metals. A finger may be plunged for a moment into liquid air with impunity, notwithstanding its low temperature, this being due to the formation of a non-conducting layer of gas between the skin and the liquid, which passes into a spheroidal state, similar to that of a drop of water poured on to a red-hot iron. Many chemical reactions which proceed at the ordinary temperature do not take place at the temperature of liquid air (see Introduction, p. 34).^{49a}

Turning to the other components of air (besides N_2 , O_2 , H_2O , and CO_2) the first to be mentioned is **Argon**, Ar (or sometimes A), whose discovery (1894) by Rayleigh and Ramsay has already been described. When Rayleigh discovered that the nitrogen remaining from air after the removal of O_2 , H_2O , and CO_2 was heavier (by $\frac{1}{200}$) than nitrogen prepared from any of its compounds (with oxygen, hydrogen, metals, or carbon), no doubt remained that the nitrogen of the air contained some other gas heavier than nitrogen. To separate this gas it was necessary to convert the nitrogen into some of its non-gaseous compounds, as the new gas evidently did not enter into the composition of any of the compounds formed by nitrogen.⁵⁰ The following two methods were adopted for this purpose: (1) oxidation of the nitrogen and (2) absorption of the nitrogen by metallic magnesium.

⁴⁸ At low temperatures chemical reaction often becomes so feeble (or even ceases altogether) that only the negative side of the question is evident; but this aspect of the subject cannot explain much, because the substances become so hard that they lose the mobility of parts necessary for chemical reaction. But as the oxygen in liquid air is compressed it supports combustion with particular energy (for instance, a smouldering cigarette bursts into flame). This has even been taken advantage of for causing explosions, as a piece of wadding or charcoal moistened with liquid air (especially if it be rich in oxygen) gives a violent explosion if it is set fire to by a spark or pistol-shot. Owing to the cheapness of liquid air this method has its economical advantages.

⁴⁹ The increase in intensity of phosphorescence at low temperatures (paraffin, bone, &c.) is mentioned in Chap. II., note 32.

^{49a} There can be no doubt that the preparation of liquid air on a large scale may prove most valuable for many purposes, and especially for obtaining air rich in oxygen at a low price and for producing extreme cold.

⁵⁰ Rayleigh and Ramsay made many most interesting experiments before they succeeded in isolating argon, proving the substance they were seeking to be heavier than nitrogen and quite distinct from it in its properties. Thus they divided air by diffusion (through a porous clay tube) into a lighter (diffusive) portion and a heavier residue, and obtained nitrogen from both (by absorbing the oxygen with copper). It was found that the nitrogen which diffused through the tube was lighter than the residue, which had therefore accumulated the heavier unknown substance.

Cavendish (1786) knew that the nitrogen of the air, under certain conditions and especially by the action of an electric discharge in the presence of alkalies or in the explosion of detonating gas,⁵¹ can be converted into nitric acid if a sufficient amount of oxygen (and moisture)

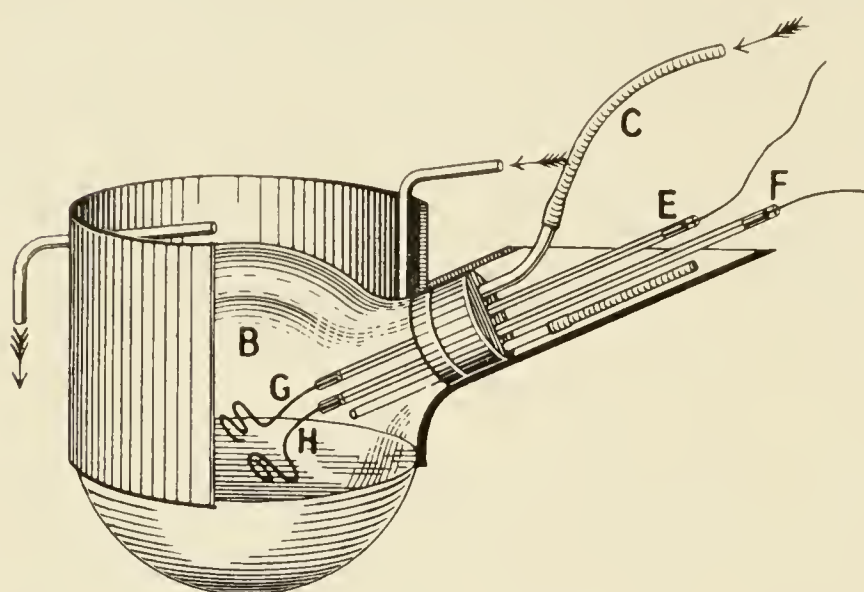


FIG. 47.—Apparatus for converting the nitrogen of the air (by the help of added oxygen) into nitric acid. Through C passes air mixed with oxygen. E G and F H are conductors from a Ruhmkorff's coil. The flask B contains a solution of caustic soda, which absorbs the nitric acid formed by the sparks; it is cooled by means of water.

be added to it; and he also observed that a portion of the nitrogen is not converted into nitric acid.⁵² After conversion into nitric acid, that is, after oxidation, the nitrogen can be easily removed (by means of alkalies, which form salts of nitric acid); and if excess of oxygen was taken, this also can be easily removed by passing it over red-hot copper.⁵³

Still this method is complicated, and it was therefore abandoned in favour of the method of absorption by finely powdered magnesium.⁵⁴ When heated, this powdered magnesium converts all the

⁵¹ See note 9.

⁵² Cavendish evidently had argon and its associates in this portion, but the small quantity of the residue probably prevented him from investigating the residual gas more closely.

⁵³ It is most important to note that Rayleigh and Ramsay obtained argon not only from the nitrogen of the air but also from nitrogen obtained from its compounds, although in the first case more than 1 vol. of argon (and its associates; see further) was given by 100 vols. of nitrogen, whilst in the second they only obtained 0.1 vol. The authors explain the presence of argon in the second instance by the fact that they collected the gas over water which might have contained argon in solution. Until this is verified it may be assumed that argon is capable of being formed from nitrogen in some way or another. This view is mentioned in the succeeding notes.

⁵⁴ Magnesium in the form of powder may be bought. Hempel advises mixing it with unslaked lime. Small pieces (thin leaves) of metallic sodium are also sometimes mixed with the magnesium, but the best plan is to add metallic lithium, which absorbs nitrogen with avidity. The magnesium in one of these forms is placed in an iron tube (unsoldered) and heated, and dry air (without CO₂) is then passed over it. The oxygen of the air is absorbed by the magnesium before the nitrogen. In order to absorb all the nitrogen, the gaseous residue (impure argon) must be passed over the magnesium several times until the spectrum (obtained by electric sparks of high intensity) no longer exhibits the characteristic lines of nitrogen. And as the residue of argon is small, and the intricate apparatus employed in its preparation must necessarily embrace a considerable gaseous volume which increases with the number of tubes of magnesium employed, the apparatus is constructed in such a manner as to cause the residue of gas to repeatedly pass over one and the same tube containing magnesium. This may be done in several

nitrogen into solid non-volatile nitride of magnesium, N_2Mg_3 , without absorbing the argon.⁵⁵ The residue, which is left unabsorbed by the magnesium, is a gas having a density of about 20 compared with that of hydrogen, whilst the densities of nitrogen and oxygen are 14 and 16 respectively. A similar gaseous residue, which is not absorbed either by ordinary solutions of reagents (alkalies, acids, salts), or by copper, magnesium, lithium, or other incandescent metals, is obtained from the air (formerly in solution) expelled by boiling from ordinary and sea water and from the water of many mineral springs (in the Pyrenees, Iceland, Germany, &c.); and here the amount of this gaseous residue is even greater than in ordinary air, which gives about 7 litres of residue per 1,000 litres. This residue,⁵⁶ when cooled by liquid air and evaporated under a low pressure (i.e., at about -200°), is entirely converted into a liquid (a portion, however, crystallising, especially at the temperature of liquid hydrogen). If this liquid is evaporated under the ordinary pressure (760 mm.) a portion of it comes over below -186° , and this portion contains helium and neon, of which mention will be made later on, while a portion which remains liquid at temperatures considerably above -186° contains krypton and xenon (see below). The main portion of the residue, however, distils over at about this temperature, and that portion which boils between -185° and -187° (under a pressure of 760 mm.) is true argon.⁵⁷ Air contains about 0.7 per cent. of argon by volume, and somewhat less than 0.2 per cent. of its associates, helium, neon, krypton, and xenon. Argon readily solidifies into a colourless mass, like ice, at about -190° under the atmospheric pressure.⁵⁸ In a gaseous state, argon is 19.8 times

ways, but it is best to make the residual gas return to the point from which it originally entered the tube with magnesium. For this purpose a small mercury aspirator (Chap. II., note 16) is placed at the end of the tube and draws the gas through a glass tube back to that containing the magnesium. As it travels along this path the gas meets two platinum wires soldered into the glass tube, through which electric sparks are passed for exhibiting the spectrum. The mercury falling into the funnel of the aspirator compels the gas to pass once more along the magnesium tube which is furnished with a metallic mixer, worked from time to time by hand, to stir the magnesium and bring fresh surfaces into contact with the gas.

⁵⁵ Professor A. P. Lidoff (1902) showed that this method of absorbing nitrogen may even be employed for the analytical determination of nitrogen by weight.

⁵⁶ This residue was at first considered to be pure argon (1894–1895), but it was afterwards (chiefly owing to the researches of Ramsay and Travers) found to be a mixture of at least five gases—helium, neon, argon, krypton, and xenon.

⁵⁷ As argon has not yet been brought into a state of combination, its further purification is impossible. It is proved, however, to be a uniform substance by the fact that its boiling-point is constant and that diffusion (through porous diaphragms) gives portions of similar density.

⁵⁸ The critical temperature of argon is about -117° and the critical pressure about 53 atmospheres.

heavier than hydrogen,⁵⁹ and in a liquid state (at -186°) 1.5 times heavier than water.⁶⁰ Although so well characterised in its physical properties, argon is distinguished in a chemical sense by such inactivity and immutability that in this respect it stands alone. All endeavours to bring it into chemical reaction have as yet been fruitless.⁶¹ This is all the more remarkable because argon (and its associates) is contained, together with nitrogen,⁶² in a fairly stable condition in certain (especially Scandinavian) minerals containing uranium, tantalum, yttrium, and other rare metals; for instance, in uranite, cleveite, monazite, eshenite, fergusonite, &c. If these minerals are slightly heated, they give off water and carbonic anhydride, but no nitrogen or argon, or their associates. These are only given off by strongly heating (to the temperature at which ordinary glass becomes soft) the minerals with sulphuric acid, or, better still, with acid sulphate of potassium (KHSO_4) or bichromate of potassium ($\text{K}_2\text{Cr}_2\text{O}_7$). If all the air be first exhausted by a Sprengel pump, the gases may be easily collected as they pass over. These gases generally consist of nitrogen, argon, and helium. Previous to Ramsay's discovery they were considered to be nitrogen. It is

⁵⁹ In Chap. XIV., note 7, it is shown that k , or the ratio of the two specific heats (at constant volume and at constant pressure), decreases as the complexity of the molecules of a gas, that is, as the number of atoms in the molecule increases. For gases containing 1 atom in the molecule the ratio is about 1.6–1.8; for 2 atoms, about 1.4; for 3, 1.3, and so on. This ratio was determined for argon (Rayleigh, Dorn) and found to be $=1.67$; from which it is concluded that its molecule is composed of one atom, like that of mercury, i.e., that argon is an element and that its molecule contains 1 atom. However, this cannot be considered as proved, because the value of k varies considerably for gases having the same number of atoms in the molecule, and greatly depends upon the range of temperature and apparently on the store of chemical energy (for instance, for chlorine, Cl_2 , k is less than for N_2 , CO , &c.), which we need not consider further here.

⁶⁰ The luminous spectrum given by the gas when an electric discharge of high intensity is passed through it (between two platinum wires in a Geissler or Plucker tube; see Chap. XIII.) is very important for characterising and determining the individuality of argon and its associates, helium, neon, krypton, and xenon. The spectra of argon and its associates (and also of some other gases) vary with the intensity of the electricity and with the pressure of the gas in which the discharge takes place. The characteristic lines for argon (Crookes, Dorn, &c.) are two red ones with wave lengths of 707 and 696 millionths of a millimetre (thousandths of a micron).

⁶¹ However, Berthelot obtained some argon from Ramsay in 1895, and subjected it to a silent discharge in a vessel together with benzene, C_6H_6 , and observed that the argon was absorbed and gave a substance similar to that given by nitrogen under like conditions. It is not known if the argon was perfectly pure, and no further explanations have been published on this subject.

⁶² It is not known in what form of combination or state the argon, helium, and other gases are present in cleveite, eshenite, and other minerals. It is not even known if they form an essential component of these minerals or if their presence is due to some impurity. Owing to the rarity of these minerals and the small amounts of argon, &c. obtained from them, there yet remains much to be done in this province of research, and many interesting data are yet to be looked for.

evident that the gases are held in the minerals in the form of somewhat stable compounds (decomposed, however, by sulphuric acid, &c.), and not simply in a state of absorption, for absorbed gases pass over of themselves when heated *in vacuo*; but neither argon, nor helium, nor their associates can be driven off in this manner. The absorption of argon by water, on the other hand, takes place with greater facility than that of nitrogen, about four volumes of argon being dissolved by 100 volumes of water at the ordinary temperature and pressure (almost the same as oxygen).

Thus argon must be regarded as a peculiar gas distinguished by its great chemical inactivity, but possessing perfectly defined physical properties, among which a typical spectrum must also be noted (see note 60). And as typical spectra chiefly belong to simple bodies,⁶³ argon is placed among their number, although the chief characteristics of simple bodies, namely, the independence and individuality of their corresponding compounds, are not exhibited by argon.⁶⁴ However, it is quite possible to imagine a class of elements which do not combine with hydrogen or oxygen to form acids or bases, just as many elements are known which do not combine with hydrogen, while fluorine does not combine with oxygen to form saline substances. If such be the case, we have the right to form a special **group of the argon elements**, including helium, He, neon, Ne, argon, Ar, krypton, Kr, and xenon Xe; not only because they accompany each other in the nitrogen of the atmosphere, and are perfectly analogous to each other in their inertness and incapacity for entering into combination in the ordinary way, or for forming compounds more or less resembling bases, acids, or salts, but

⁶³ In Chap. XIII. we shall see, however, that compound bodies have also their spectra, if they can be subjected to the necessary degree of incandescence.

⁶⁴ Neither are there any reasons for considering argon as a compound substance, although when it was first discovered (1894) I had my reasons for considering it a polymeride of nitrogen, N_3 , standing in the same relation to nitrogen, N_2 , as ozone, O_3 , does to oxygen, O_2 (see last edition of *Principles of Chemistry*), but formed with the evolution of heat (ozone is formed with the absorption of heat). If argon and its associates (helium, &c.) be regarded as individual chemical elements, then, owing to their incapacity to form saline compounds of the type RX_n (see Chap. XV.), they must be placed in a special, so to speak, zero group preceding the first group, the elements of which give RX , and forming a transition stage towards the halogens (group VII. giving hydrogen compounds of the type RX and oxygen compounds of the type RX_7). This view, which answers to what Ramsay stated to me personally (March 19, 1900) is in accordance with the fact that argon and its analogues contain one atom in their molecule, which gives the possibility of determining the atomic weight from the density, for the atomic weights of such elements referred to that of hydrogen (Chap. VII.) are approximately equal to twice the densities of the gases also referred to that of hydrogen. Thus if the density of argon is 19.8, its atomic weight must be near to 39.6. And the periodic law (Chap. XV.) requires that the order in which the elements stand according to their atomic weights should correspond with their properties, and therefore the atomic weights of argon and its analogues should be greater than the atomic weights of the halogens of

also because ⁶⁵ this group of argon elements is exactly similar (even in the values of the atomic weights) to the other most characteristic groups of the elements spoken of more fully in Chap. XV.

The analogues of argon have all been found, as already mentioned, in air; that is, in its nitrogen; but they also accompany nitrogen and argon in the above-named minerals, such as cleveite, and **Helium**, $\text{He}=4.0$, was first obtained by Ramsay in 1895 by heating cleveite with sulphuric acid. The history of helium, however, begins before its discovery was an accomplished fact, and it had even been named, for Lockyer, from observations on the spectrum of the solar protuberances (Chap. XIII.), foretold the existence of an element giving a bright pale yellow line (wave length 587.0 thousandths of a micron), and a feebler green line (wave length 508). Helium may be separated from argon, nitrogen, and the other argon gases, owing to its being lighter than any of them, and therefore passing through porous partitions in larger quantity. More-

group VII., but less than those of the alkali metals of group I. This is, if not quite, at all events very nearly confirmed by their *observed* densities.

	He	Ne	Ar	Kr	Xe
Density (H=1)	2.0	9.95	19.8	40.6	63.5

Therefore taking hydrogen = 1 (and we take it = 1.008) the atomic weights of these elements will be:

He = 4:	Ne = 19.9:	Ar = 39.6:	Kr = 81.2:	Xe = 127.0
helium	neon	argon	krypton	xenon

These values of the atomic weights of the halogens of group VII. and those of the alkali metals of group I. (taking H = 1) are:

Group VII.	F	Cl	Br	I
	18.9	35.2	79.4	125.9
I. Li	Na	K	Rb	Cs
7.0	22.9	38.9	84.8	132.0

All the analogues of argon (judging by their densities) have, therefore, greater atomic weights than the corresponding elements of group VII., and smaller atomic weights than those of the alkali metals (argon presents a slight discrepancy, as, judging from Cl and K, its atomic weight should be about 37, that is, its density should be 18.5 instead of 19.8. This leads one to think that argon still includes some other gas of high density in admixture with it). Moreover, we find that F, Cl, Br, and I exhibit a resemblance to each other similar to that shown by Li, Na, K, Rb, and Cs, or He, Ne, Ar, Kr, and Xe. The parallel goes still further, for the first members of all three groups have certain peculiarities, as we shall see later. These considerations support the idea of the elementary character of the analogues of argon, and indicate to us their position in regard to the other elements. Still, it is impossible to be quite sure of the true nature of these gases until some of their compounds (for instance, of the kind present in cleveite, fergusonite, &c.) have been obtained. Professor Ramsay himself first informed me (1900, see above) of the position occupied by the analogues of argon in the periodic system between the halogens and the metals of the alkalies; later Professor Ramsay published a paper on the subject, and in 1902 communications on the same subject were published by N. N. Beketoff, Piccini, and others. For my part, when I saw the above regularity, I became more inclined than before to regard argon and its analogues with their peculiar combination of properties as elementary substances standing, not in group VIII., as some think, but forming a special (zero) group.

⁶⁵ As explained in the preceding note

over it does not pass into a liquid state under the action of cold, even at the temperature produced by liquid hydrogen,⁶⁶ and if helium is present in admixture with the other argon gases it dissolves in them when they liquefy, but the solution parts with almost pure helium at -250° (in liquid hydrogen) in a vacuum. The density of helium is only twice that of hydrogen, so that it is the lightest of all gases except hydrogen. In other respects helium is exactly like argon.⁶⁷ **Neon**, $\text{Ne}=19.9$, which accompanies helium in air and has the density 9.95, differs in the free state from helium in the fact that it liquefies in the cold produced by liquid air, and remains liquid at the temperature of liquid hydrogen under a low pressure; it boils below -186° (that is, is more volatile than argon) and gives a spectrum with brilliant reddish-orange lines (650, 641). Among the liquefiable argon gases, two more gases occur in those portions of liquid air which evaporate with the greatest difficulty, namely, **Krypton**, $\text{Kr}=81.8$, and **Xenon**, $\text{X}=128$, discovered by Ramsay and Travers. They are also looked upon as simple bodies, but they boil at a higher temperature than argon. The spectrum of the former is greenish yellow (wave lengths of the most brilliant lines,⁶⁸ 558, 477, 474, and 450 thousandths of a micron), while that of the latter is blue (wave lengths 492, 481, 474, 467, 463). The density of krypton is 40.6 and that of xenon, 63.5; so that these gases are much heavier than all the other gases in the atmosphere (the density of CO_2 being, for example, 22). However, they are present in such minute quantities in the atmosphere that it requires great perseverance to extract even the smallest amount of such a gas as xenon, for only four volumes of it have been procured from 600 million volumes of air. The amount of krypton in air is much greater, but still far less than that of argon.

If these five argon gases be compared, they are all seen to be of very rare occurrence on the earth, to be chemically inactive, and to present a distinct sequence in the variation of their properties.

	He.	Ne	Ar	Kr	Xe
Density	1.98	9.95	19.96	40.88	64
Boiling-point: below	-262°	-239°	-187°	-152°	-109° ^{68a}

⁶⁶ At first it was thought that helium could be converted into a liquid at low temperatures, but now it appears that this is only true for impure helium.

⁶⁷ The ratio of the specific heats is about 1.66, as with argon. Helium, as an unliquefiable gas, is used in thermometers for determining the lowest possible temperatures.

⁶⁸ Similar green spectrum lines are observed in the spectrum of the aurora borealis.

^{68a} Since the spectrum lines of helium have been observed in the sun and in certain stars, and those of krypton and the others in the corona, zodiacal light, and aurora borealis, these gases may be assumed to enter into the composition of interplanetary space and to have some connection with the substance which forms 'ether.'

We will now consider the few remaining gases and vapours occurring in ordinary air.⁶⁹

The researches of Saussure (1806), Boussingault (1833), and especially of A. Gauthier (1899–1900) showed that the air, even at high altitudes, always contains about 0·02 per cent. (by volume) of **hydrogen** and a variable amount (more in cities and forests, less on mountains) of hydrocarbons, such as marsh gas, evolved in the decay of plants (Chapter VIII).^{69a} Their presence is shown by the fact that when air, which has been quite freed from water and carbonic anhydride, is passed over a long layer of red-hot copper oxide it again gives these substances (see note 22) in the proportion of 1 part by weight of hydrogen to generally less than 3 parts by weight of carbon, or with mountain air even ten times less; while marsh gas, CH_4 , which contains more hydrogen than any other known compound of carbon, contains 3 parts by weight of hydrogen to 1 part of carbon. As the hydrogen of the atmosphere may partly oxidise to form water, and must partly pass into the interplanetary space, owing to its diffusive properties (Chap. I., notes 34 and 35), it is evident that its presence in air cannot be explained unless constant sources for its formation exist in nature. According to A. Gauthier, such a source is found in rocks, like the granites, as these evolve hydrogen (in small quantity) when acted upon by aqueous vapour in a vacuum and when heated to redness with phosphoric anhydride. Therefore there is reason to think that the rock formations of the earth cause a constant flow of hydrogen to the atmosphere.⁷⁰

⁶⁹ Of course in special cases, when particular gases or vapours, for instance, SO_2 , H_2S , &c., are evolved, they may pass into the surrounding air, but they either undergo change or disperse.

^{69a} Besides the ten-thousandths (by volume) of hydrogen and hydrocarbons, Gauthier found small traces (especially in the air of towns), or some millionths by volume, of carbon monoxide, CO , as a product of imperfect combustion. It was determined by its reaction (at 60° – 80°) with iodic anhydride, I_2O_5 (previously calcined to drive off all moisture), which, as Ditte showed, gives iodine and carbonic anhydride, $\text{I}_2\text{O}_5 + 5\text{CO} = \text{I}_2 + 5\text{CO}_2$. The resultant iodine and carbonic anhydride are easily collected, the former by powdered copper and the latter by washing with caustic baryta, which absorbs the slightest traces of CO_2 from any gaseous mixture.

⁷⁰ The investigation of liquid air and the discovery of small amounts of hydrogen, argon, helium, &c., in it have been accomplished during the last few years by means of extensive and very careful researches, thus proving in a most instructive manner that more and more new objects may be found in all that surround us if we follow a method of careful research based upon the logical study of facts already known. I make this remark for the benefit of those beginners who may be discouraged by the vast stores of scientific research, and may imagine that there is nothing left for them to discover. But as a matter of fact there remains to be discovered far more than has as yet been made known. Newton rightly said that we have only become acquainted with the grains of sand on the shores of the infinite ocean of nature. These words of the great investigator are, I think, as true now after 200 years of indefatigable labour as they were then, for

The presence of **ammonia**, a compound of nitrogen and hydrogen, in the air is indicated by the fact that all acids exposed to the air absorb ammonia from it after a time. De Saussure observed that aluminium sulphate is partially converted by air into a double sulphate of ammonium and aluminium, the so-called ammonia alum. Quantitative determinations have shown that the amount of ammonia⁷¹ contained in air varies at different periods. However, it may be accepted that 100 cubic metres of air do not contain less than 1 or more than 5 milligrams of ammonia.⁷² The air in those places where animal substances undergoing change are accumulated, and especially that of stables, generally contains a much greater quantity of this gas. This is the reason of the peculiar pungent smell noticed in such places. Moreover, as we shall learn in the following chapter, ammonia combines with acids, and should therefore be found in air in the form of such combinations, since air contains carbonic and nitric acids.

The presence of **nitric acid** in air is proved without doubt by the fact that rain-water contains an appreciable amount of it.

Further (as already mentioned in Chap. IV.), air contains a small and variable amount of ozone and hydrogen peroxide and nitrous acid (and its ammonia salt), i.e., substances having a direct oxidising action (for instance, upon iodised starch-paper), but these are present in very small quantities⁷³ (Chap. IV.).

Besides substances in a gaseous or vaporous state,⁷⁴ there is always found a more or less considerable quantity of solid substances as **dust**, and also salts and organic matter not enumerated above. If a linen surface, moistened with an acid, be placed in perfectly pure air, the washings are found to contain sodium, calcium, iron, and potassium.⁷⁵ the few grains, or even stones, we have gathered have only revealed fresh depths in the unknown.

⁷¹ Schloesing studied the equilibrium of the ammonia of the atmosphere and of the rivers, seas, &c., and showed that the amount of the gas is interchangeable between them. The ratio between the amount of ammonia in a cubic metre of air and in a litre of water at $0^{\circ}=0.004$, at $10^{\circ}=0.010$, at $25^{\circ}=0.040$ to 1, and therefore in nature there is a state of equilibrium in the amount of ammonia in the atmosphere and waters.

⁷² It is remarkable that it occurs in greater quantity on mountains than in valleys (the same thing is observed with ozone and even CO_2).

⁷³ Though being formed in the air, these oxidising substances (N_2O_3 , ozone, and hydrogen peroxide) at the same time rapidly disappear from it by causing the oxidation of substances capable of being oxidised. Owing to this instability their amounts vary considerably, and, as would be expected, they are met with to an appreciable extent in pure air, whilst their amount decreases to zero in the air of cities and especially of dwellings, where there is a maximum of substances capable of oxidation and a minimum of conditions favouring the formation of such bodies.

⁷⁴ Amongst them we may mention iodine and alcohol, $\text{C}_2\text{H}_6\text{O}$, which Müntz found to be always present in air, soil, and water, although in minute traces only.

⁷⁵ A portion of the atmospheric dust is of cosmic origin: this is indisputably proved by the fact that it contains metallic iron, as do meteorites. Nordenskiöld found iron in

Linen moistened with an alkali absorbs carbonic, sulphuric, phosphoric, and hydrochloric acids. Further, the presence of organic substances in air has been proved by a similar experiment. If a glass globe be filled with ice and placed in a room where are a number of people, the presence of organic substances, such as albuminous bodies, may be detected in the water which condenses on the surface of the globe. It may be that the miasmata causing infection in marshy localities, hospitals, and in certain epidemic diseases, proceed from the presence of such substances in the air (and especially in water, which contains many micro-organisms), as well as from the presence of germs of lower organisms in the air in the form of a minute dust. Pasteur proved the existence of such germs in the air by the following experiment: He placed in a glass tube some gun-cotton (pyroxylin), which has the appearance of ordinary cotton and is soluble in a mixture of ether and alcohol, forming the so-called collodion. A current of air was passed through the tube for a long time, after which the gun-cotton was dissolved in a mixture of ether and alcohol. An insoluble residue was thus obtained which actually contained the germs of organisms, as was shown by microscopical observations, and by their capacity of developing under favourable conditions into organisms (mould, &c.). The presence of these germs determines the property possessed by air of bringing about the processes of putrefaction and fermentation—that is, the fundamental alteration of organic substances accompanied by an entire change in their properties. The appearance of lower organisms, both vegetable and animal, is always to be observed in these processes. Thus, for instance, in the process of fermentation, when, for example, wine is procured from the sweet juice of grapes, a sediment separates out which is known under the name of lees, and contains peculiar yeast organisms. Germs are required before these organisms can appear.⁷⁶ These germs are floating in the air, and fall therefrom into the sweet fermentable liquid. Finding themselves under favourable conditions, the germs develop into organisms, they are nourished at the expense of the organic substances present, and during their growth change and destroy these substances and bring about fermentation and putrefaction. This explains why, for instance, the juice of the grape when contained the dust covering snow, and Tissandier detected it in every kind of air, although naturally in very small quantities.

⁷⁶ The idea of the spontaneous growth of organisms in a suitable medium, although still upheld by many, has been discarded since the work of Pasteur and his followers (and to a certain extent of his predecessors), because it has been proved how, when, and whence (from the air, water, &c.) the germs appear, and that neither fermentation nor infectious diseases can take place without them; and chiefly because it has been shown that any change accompanied by the development of the organisms introduced may be brought about at will by the introduction of the germs into a suitable medium.

in the skin of the fruit, which allows access of the air but is impenetrable to the germs, does not ferment or change so long as the skin remains intact. It is for this reason also that animal substances when kept out of contact of air may be preserved for a great length of time. Preserved foods for long sea voyages are kept in this way.⁷⁷ It is hence evident that, however infinitesimal the quantity of germs carried in the atmosphere may be, they have an immense significance in nature.⁷⁸

Thus we see that air contains a great variety of substances. The nitrogen, which is found in it in the largest quantity, has the least influence on those processes which are accomplished by the action of air. The oxygen, which is met with in a lesser quantity than the nitrogen, takes, on the contrary, a very important part in a number of reactions: it supports combustion and respiration, it brings about decomposition and every process of slow oxidation. The part played by the moisture of air is well known; without it and its precipitations the earth would be a desert. The carbonic anhydride, which is met with in still smaller quantities, has an immense significance in nature, inasmuch as it serves for the nourishment of plants. The importance of the ammonia and nitric acid is very great, because they are the sources of the nitrogenous substances constituting an indispensable element in all living organisms. And, lastly, the infinitesimal quantity of germs also has a great significance in a number of processes. Thus it is not the quantitative but the qualitative relations of the component parts of the atmosphere which determine its importance in nature.⁷⁹

⁷⁷ In confirmation of the fact that putrefaction and fermentation depend on germs carried in the air, we may cite the circumstance that poisonous substances destroying the life of organisms prevent or hinder the appearance of the above processes. Air which has been heated to redness or passed through sulphuric acid no longer contains the germs of organisms (sterilisation), and loses the power of producing fermentation and putrefaction.

⁷⁸ Their presence in the air is naturally due to the diffusion of germs into the atmosphere, and owing to their microscopical dimensions; they hang, as it were, in the air by virtue of the large surface they possess compared with their weight. In Paris the amount of dust suspended in the air amounts to from 6 (after rain) to 23 grams per 1,000 cm. of air.

⁷⁹ We see similar cases everywhere. For example, the predominating mass of sand and clay in the soil takes scarcely any chemical part in the economy of the soil in respect to the nourishment of plants. The plants by their roots search for substances which are diffused in comparatively small quantities in the soil. If a large proportion of these nourishing substances is removed, then the plants will not develop in the soil, just as animals die in oxygen. There exists everywhere a medium in things, determined by equilibrium. The Russian proverb says, 'Too much salt or too little salt is alike an evil.' It is the same in political and social relations.

Air, being a mixture of various substances, may suffer considerable **changes** in consequence of incidental circumstances. It is particularly necessary to remark those changes in the composition of air which take place in dwellings and in various localities where human beings have to remain during a lengthy period of time. The respiration of human beings and animals alters the air.⁸⁰ A similar deterioration of air is produced by the influence of decomposing organic substances, and especially of substances burning in it, and then the amount of oxygen decreases while the proportion of noxious impurities increases.⁸¹ Hence it is necessary to have regard to the purification of the air of dwellings. The renewal of air, the replacing of respired by fresh air, is termed

⁸⁰ A man in breathing burns about 10 grams of carbon per hour—that is, he produces about 880 grams, or (as 1 cub.m. of carbonic anhydride weighs about 2,000 grams) about $\frac{5}{12}$ c.m. of carbonic anhydride. The air coming from the lungs contains 4 per cent. of carbonic anhydride by volume. The exhaled air acts as a direct poison, owing to the presence of this gas and other impurities.

⁸¹ For this reason candles, lamps, and gas change the composition of air almost in the same way as respiration. In the burning of 1 kilogram of stearin candles, 50 cubic metres of air are changed as by respiration—that is, 4 per cent. of carbonic anhydride will be formed in this volume of air. The respiration of animals and the exhalations from their skins and especially from their intestines and the transformations taking place in these bodies contaminate the air to a still greater extent, because they introduce into it other volatile substances besides carbonic anhydride. At the same time that carbonic anhydride is formed the amount of oxygen in the air decreases, and there is noticed the appearance of miasmata which occur in but small quantity, but which are noticeable in passing from fresh air into a confined space full of such adulterated air. The researches of Schmidt and Leblanc and others show that even when the percentage of oxygen in air is reduced, as a result of respiration, merely from 20·9 to 20·6, the air becomes noticeably less fit for respiration, and that the heavy feeling experienced in such air increases with a further diminution in the percentage of oxygen. It is difficult to remain for a few minutes in air containing only 17·2 per cent. of oxygen. These observations were chiefly obtained by observations on the air of mines at different depths below the surface. The air of theatres and buildings full of people also proves to contain a deficiency of oxygen: it was found on one occasion that at the end of a theatrical representation the air in the stalls contained 20·75 per cent. of oxygen, whilst that in the upper part of the theatre contained only 20·36 per cent. The amount of carbonic anhydride in the air may be taken as a measure of its purity (Pettenkofer). When it reaches 1 per cent. it is very difficult for human beings to remain long in such air, and it is necessary to set up a vigorous ventilation for the removal of the adulterated air. In order to keep the air in dwellings in a uniformly good state, it is necessary to introduce *at least* 10 cubic metres of fresh air per hour per person. We saw that a man exhales about five-twelfths of a cubic metre of carbonic anhydride per day. Accurate observations have shown that air containing 0·1 per cent. of exhaled carbonic anhydride (and consequently also a corresponding amount of the other substances evolved together with it) is not felt to be oppressive; and therefore the five-twelfths of a cubic metre of carbonic anhydride should be diluted with 420 cubic metres of fresh air if it be desired to have not more than 0·1 per cent. (by volume) of carbonic anhydride present. Hence a man requires 420 cubic metres of air per day, or 18 cubic metres per hour. With the introduction of only 10 cubic metres of fresh air per hour per person, the proportion of carbonic anhydride may reach 0·2 per cent., and the air will not then be of the requisite freshness.

‘ventilation,’⁸² and the removal of foreign and injurious admixtures from the air is called ‘disinfection.’⁸³ The accumulation of all kinds

⁸² The **ventilation** of inhabited buildings is most necessary, and is even indispensable in hospitals, schools, and similar buildings. In winter it is carried on by the so-called calorifiers or stoves heating the air before it enters. The best kind of calorifiers in this respect are those in which the fresh cold air is led through a series of flues heated by the hot gases coming from a stove. In ventilation, particularly during winter, care is taken that the incoming air shall be moist, because in winter the amount of moisture in the air is very small. Ventilation, besides introducing fresh air into a dwelling-place, must also withdraw the air already spoilt both by respiration and from other causes—that is, it is necessary to construct channels for the escape of the bad air, besides those for the introduction of fresh air. In ordinary dwelling-places, where not many people are congregated, the ventilation is maintained by natural means—by fires, crevices, windows, and various orifices in walls, doors, and windows. In mines, factories, and workrooms ventilation is of the greatest importance.

Animal vitality may, however, continue for a period of several minutes in air containing as much as 30 per cent. of carbonic anhydride if the remaining 70 per cent. consist of ordinary air; but respiration ceases after a certain time, and death may even ensue. The flame of a candle is very rapidly extinguished in an atmosphere containing from 5 to 6 per cent. of carbonic anhydride; but animal vitality can be sustained in it for a somewhat long time, although the effect of such air is exceedingly painful even to the lower animals. The presence of 1 per cent. of carbonic oxide is fatal even to cold-blooded animals. The air in the galleries of a mine where blasting has taken place is known to produce a state of insensibility resembling that produced by charcoal fumes. Deep wells and vaults not infrequently contain similar substances, and their atmosphere often causes suffocation. The atmosphere of such places cannot be tested by lowering a lighted candle into it, as these poisonous gases would not extinguish the flame. This method only suffices to indicate the amount of carbonic anhydride. If a candle keeps alight, it signifies that there is less than 6 per cent. of this gas. In doubtful cases it is best to lower a dog or other animal into the air to be tested. If CO_2 be very carefully added to air, the flame of a candle is not extinguished (although it becomes very much smaller) even when the gas is present to the extent of 12 per cent. Researches made by F. Clowes (1894) show that the flames ($\frac{3}{4}$ in. long) of different combustible substances are extinguished by the gradual addition of different percentages of nitrogen and carbonic acid to the air; the percentages sufficient to extinguish the flame being as follows (the percentage of oxygen present being given in parenthesis):

	per cent. of CO_2	per cent. of N_2
Absolute alcohol	14 (18.1)	21 (16.6)
Candle	14 (18.1)	22 (16.4)
Hydrogen	58 (8.8)	70 (6.3)
Coal gas	33 (14.1)	46 (11.3)
Carbonic oxide	24 (16.0)	28 (15.1)
Methane	10 (18.9)	17 (17.4)

The flames of all solid and liquid substances are extinguished by about the same percentage of CO_2 or N_2 , but the flames of different gases vary in this respect, and hydrogen continues to burn in mixtures which are far poorer in oxygen than those in which the flames of other combustible gases are extinguished; the flame of methane is the most easily extinguished. The percentage of nitrogen may be greater than that of carbonic anhydride. This, together with the fact that under the above circumstances the flame of a gas, before going out, becomes fainter and increases in size, indicates that the chief reason for the extinction of the flame is the fall in its temperature.

⁸³ Different so-called **disinfectants** purify the air and prevent the injurious action of

of impurities in the air of dwellings and cities is the reason why the air of mountains, forests, seas, and non-marshy localities covered with vegetation or snow is distinguished for its freshness and for its beneficial action.⁸⁴

certain of its components by changing or destroying them. Disinfection is especially necessary in those places where volatile substances are evolved into the air in considerable quantity, and where organic substances are decomposed; for instance, in hospitals, closets, &c. The numerous disinfectants employed are of the most varied nature. They may be divided into oxidising, antiseptic, and absorbent substances. To the oxidising substances used for disinfection belong chlorine and also various substances evolving it, because chlorine in the presence of water oxidises the majority of organic substances. This is why chlorine is used as a disinfectant for Siberian plagues. Further, to this class belong the permanganates of the alkalies and peroxide of hydrogen, substances readily oxidising matters dissolved in water. These salts are not volatile like chlorine, and therefore act much more slowly, and have a much more limited sphere of action. Antiseptic substances are those which convert organic substances into such as are little prone to change, and prevent putrefaction and fermentation. They most probably kill the germs of organisms occurring in miasmata. The most important of these substances are creosote and phenol (carbolic acid), which occur in tar and are used for preserving smoked meat. Phenol is a substance little soluble in water, volatile, oily, and having the characteristic smell of smoked objects. Its action on animals in considerable quantities is injurious, but in small quantities, used in the form of a weak solution, it prevents change in animal matter. The smell of urinals, which depends on the change of excremental matter, may be easily removed by means of chlorine or phenol. Salicylic acid, thymol, common tar and especially its solution in alkalies as proposed by Nensky, &c., have the same property. Absorbent substances are of no less importance, especially as preventives, than the preceding two classes of disinfectants, inasmuch as they are innocuous. They are those substances which absorb the odoriferous gases and vapours which are emitted during putrefaction, and which are chiefly ammonia, sulphuretted hydrogen, &c. To this class of disinfectants belong charcoal, certain salts of iron, gypsum, salts of magnesia, and similar substances, as well as peat, mould, and clay. Questions of disinfection and ventilation are among the most serious problems of everyday life and hygiene. These questions are so vast that we are here able to give only a short outline of their nature.

⁸⁴ As it is often necessary in making researches of different kinds (especially such as concern combustion, respiration, &c.) to make detailed calculations based on a knowledge of the composition of ordinary air by weight and volume, I think it well to sum up here the existing data on the composition of air. First of all the component parts of air must be divided into those which are constant and those which are variable or incidental (such as the products of smoke or respiration). Among the latter, moisture must be included, because its absolute quantity (for instance, the number of grams per cubic metre) varies considerably with the temperature and degree of dryness of the air. The following calculation relates to the constant components of the air, on the assumption that dry air contains about 23.12 per cent. of oxygen by weight (with a possible variation of not more than ± 0.05 per cent.), and that a litre of such air (under normal conditions, i.e., at 0° and 760 mm. and at latitude 45°) weighs about 1.293 gm. Then it must be remembered that although hydrogen, ammonia, &c., always enter into the composition of air, they occur in but small proportions (for instance, 0.02 per cent. by vol. or 0.0018 per cent. by weight of hydrogen), and act so slightly upon the weight of a given volume of air, and on all the calculations appertaining to it, that their influence may be neglected in comparison with that of the variations in the amounts of oxygen and nitrogen. These component parts should be included under the category of 'various other components,' just as the category 'argon' also includes its associates krypton, neon, xenon, and helium. Thus the composition of dry air is:

By volume per cent.	Weight of litre at 0° and 760 mm.	Per cubic metre at 0° and 760 mm.	By weight per cent.
Oxygen—20·91	1·429	129·8	23·12
Nitrogen—78·23	1·251	978·7	75·7
Argon— (&c.)—0·80	1·78	14·2	1·10
Carbonic anhydride—0·03	1·98	0·6	0·95
Various other components—0·03	0·32	0·1	0·01
Dry air 100·000	—	1292·4	100·00

The last cipher in each of the above numbers is of doubtful accuracy, as the observations are subject to possible errors and the composition of air varies (for argon Schloesing gives 0·935 per cent. by vol.). The amount of each component part and the weight of a cubic metre of air in different cases are easily calculated from what has been said in Chap. I., note 1, that is if we know the vapour pressure p mm. of the water vapour in the air, the barometric pressure P mm. and the temperature t° ; for instance if $P = 740$, $t = 20^{\circ}$ and $p = 10$ mm. (relative moisture 57·4 per cent.), then taking the weight of a litre of aqueous vapour (under normal conditions) as 0·8 gram, we find that the volume of the aqueous vapour stands to the volume of dry air in the ratio $p : P - p$ or $10 : 740 - 10$; i.e., that a litre of air will contain 13·5 c.c. of aqueous vapour and 986·5 c.c. (or millilitres) of dry air, and as the composition by volume of the latter is known we can find the amount by volume of all the remaining components. Knowing also that a litre of aqueous vapour under normal conditions weighs 0·8 gram, and that the coefficient of expansion of gases and vapours is 0·00367, it is easy to calculate the composition by weight and also the weight of a litre, recollecting, however, that the laws of gases and vapours (Boyle's, Dalton's, &c.) are only approximate, and cannot give absolutely accurate results.

CHAPTER VI

THE COMPOUNDS OF NITROGEN WITH HYDROGEN AND OXYGEN

IN the last chapter we saw that nitrogen does not directly (i.e., under

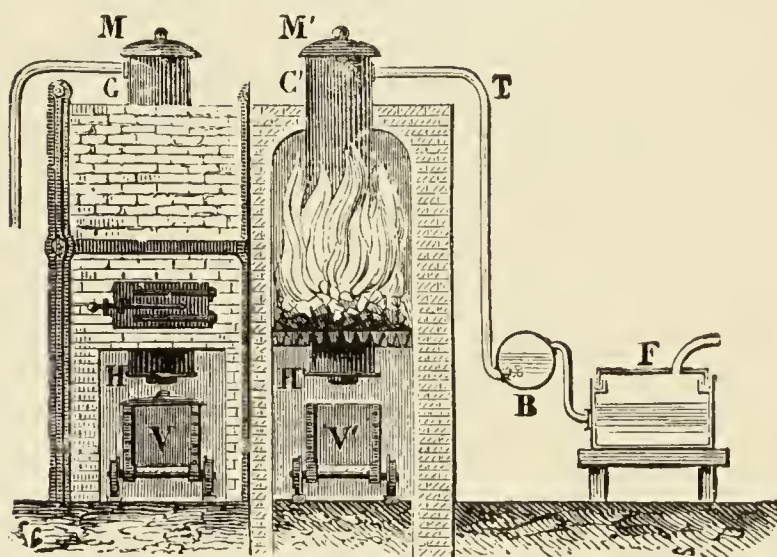


FIG. 48.—The dry distillation of bones on a large scale. The bones are heated in the vertical cylinders C (about $1\frac{1}{2}$ metre high and 30 centimetres in diameter). The products of distillation pass through the tubes T into the condenser B and receiver F. When the distillation is completed the trap H is opened, and the burnt bones are loaded into trucks V. The roof M is then opened and the cylinders are charged with a fresh quantity of bones. The ammonia water is preserved, and is used for the preparation of ammoniacal salts, as is shown in the following drawing.

ordinary conditions) combine with hydrogen or oxygen, but hydrogen and oxygen compounds of nitrogen are formed indirectly, and are even present in the atmosphere, water, and soil. Thus a mixture of nitrogen and hydrogen, in presence of hydrochloric acid gas, HCl , forms ammonium chloride, NH_4Cl , under the action of a series of electric sparks.¹ In ammonium chloride, HCl is combined with NH_3 ; consequently here we find nitrogen and hydrogen directly forming **ammonia**.² This is

the simplest typical compound of nitrogen, and therefore we shall begin with it. Almost all the **nitrogenous constituents of plants and**

¹ The ammonia in the air, water, and soil proceeds from the decomposition of the nitrogenous substances of plants and animals, and also probably from the reduction of nitrates. Ammonia is always formed in the rusting of iron. Its formation in this case depends in all probability either on the decomposition of water and on the action of the hydrogen, at the moment of its evolution, on the nitric acid contained in the air (Cloeze) or on the formation of ammonium nitrite, which takes place under many circumstances, and in its composition, NH_4NO_2 , is equal to nitrogen, N_2 + water, $2\text{H}_2\text{O}$. The evolution of vapours of ammonia compounds is sometimes observed in the vicinity of volcanoes. At a red heat nitrogen combines directly with boron, calcium, magnesium, and many other metals, and the compounds thus formed, when heated with a caustic alkali, or in the presence of water, give ammonia. These are examples of the indirect combination of nitrogen with hydrogen.

² If a silent discharge or a series of electric sparks is passed through ammonia gas, the latter is decomposed into nitrogen and hydrogen. This is a phenomenon of

animals when heated with an alkali evolve their nitrogen as ammonia. But even without the presence of an alkali the majority of nitrogenous substances, when decomposed or heated with a limited supply of air, evolve their nitrogen, if not entirely, at all events partially, in the form of ammonia. When animal substances such as skins, bones, flesh, hair, horns, &c., are heated without access of air in iron retorts, they undergo what is termed dry distillation. A portion of the resultant substances remains in the retort and forms a carbonaceous residue, whilst the other portion, in virtue of its volatility, escapes through the tube leading from the retort. The vapours given off, on cooling, form a liquid which separates into two layers: the one, which is oily, is composed of the so-called animal oils (*oleum animale*): the other, an aqueous layer, contains a solution of ammonium salts. If this solution be mixed with lime and heated, the lime takes up the elements of carbonic acid from the ammonium salts, and ammonia is evolved as a gas.³ In ancient times ammonium compounds were imported into

dissociation; that is, a series of sparks do not totally decompose the ammonia, but leave a certain portion undecomposed. One volume of nitrogen and three volumes of hydrogen are obtained by the decomposition of two volumes of ammonia. Ramsay and Young (1884) investigated the decomposition of NH_3 under the action of heat, and showed that at 500° , $1\frac{1}{2}$ per cent. is decomposed; at 600° , about 18 per cent.; and at 800° , 65 per cent.; but these results were hardly free from the influence of 'contact.' The action of a silent discharge on a mixture of nitrogen and hydrogen also gives ammonia, but not to completion.

The presence of free ammonia—that is, ammonia not combined with acids—in a gas or aqueous solution may be recognised by its characteristic smell. But many ammonia salts do not possess this smell. However, on the addition of an alkali (for instance, caustic lime, potash, or soda), they evolve ammonia gas, especially when heated. The presence of ammonia may be made visible by introducing a substance moistened with strong hydrochloric acid into its neighbourhood. A white cloud, or visible white vapour, then makes its appearance. This depends on the fact that both ammonia and hydrochloric acid are volatile, and on coming into contact with each other produce solid sal-ammoniac, NH_4Cl , which forms a cloud. This test is usually made by dipping a glass rod into hydrochloric acid and holding it over the vessel from which the ammonia is evolved. With small amounts of ammonia this test is, however, untrustworthy, as the white vapour is scarcely observable. In this case it is best to take paper moistened with mercurous nitrate, HgNO_3 . This paper turns black in the presence of ammonia owing to the formation of a black compound of ammonia with mercurous oxide. The smallest traces of ammonia (for instance, in river water) may be detected by means of the so-called *Nessler's reagent*, containing an alkaline solution of mercury in potassium iodide, which forms a brown precipitate ($\text{Hg}_2\text{NIH}_2\text{O}$) with the smallest quantities of ammonia. It will be useful here to give the thermo-chemical data (in thousands of heat units, according to Thomsen), or the quantities of heat *evolved* in the formation of ammonia and its compounds in quantities expressed by their formulæ. Thus, for instance, $(\text{N} + \text{H}_3)$ 26.7 indicates that 14 grams of nitrogen in combining with 3 grams of hydrogen develop sufficient heat to raise the temperature of 26.7 kilograms of water 1° . $(\text{NH}_3 + n\text{H}_2\text{O})$ 8.4 (heat of solution); $(\text{NH}_3, n\text{H}_2\text{O} + \text{HCl}, n\text{H}_2\text{O})$ 12.3; $(\text{N} + \text{H}_4 + \text{Cl})$ 90.6; $(\text{NH}_3 + \text{HCl})$ 41.9.

³ The same ammonia water is obtained, although in smaller quantities in proportion to the weight taken, in the dry distillation of plants and of coal, which consists of the remains of fossil plants. In all these cases the ammonia proceeds from the destruction

Europe from Egypt, where they were prepared from the soot obtained in the employment of camel's dung as fuel in the locality of the temple of Jupiter Ammon (in Libya), and therefore the salt obtained was called 'sal-ammoniacum,' from which the name of 'ammonia' is derived. At the present time ammonia is obtained almost exclusively, on a large scale, from the products of the dry distillation of coal. The ammoniacal

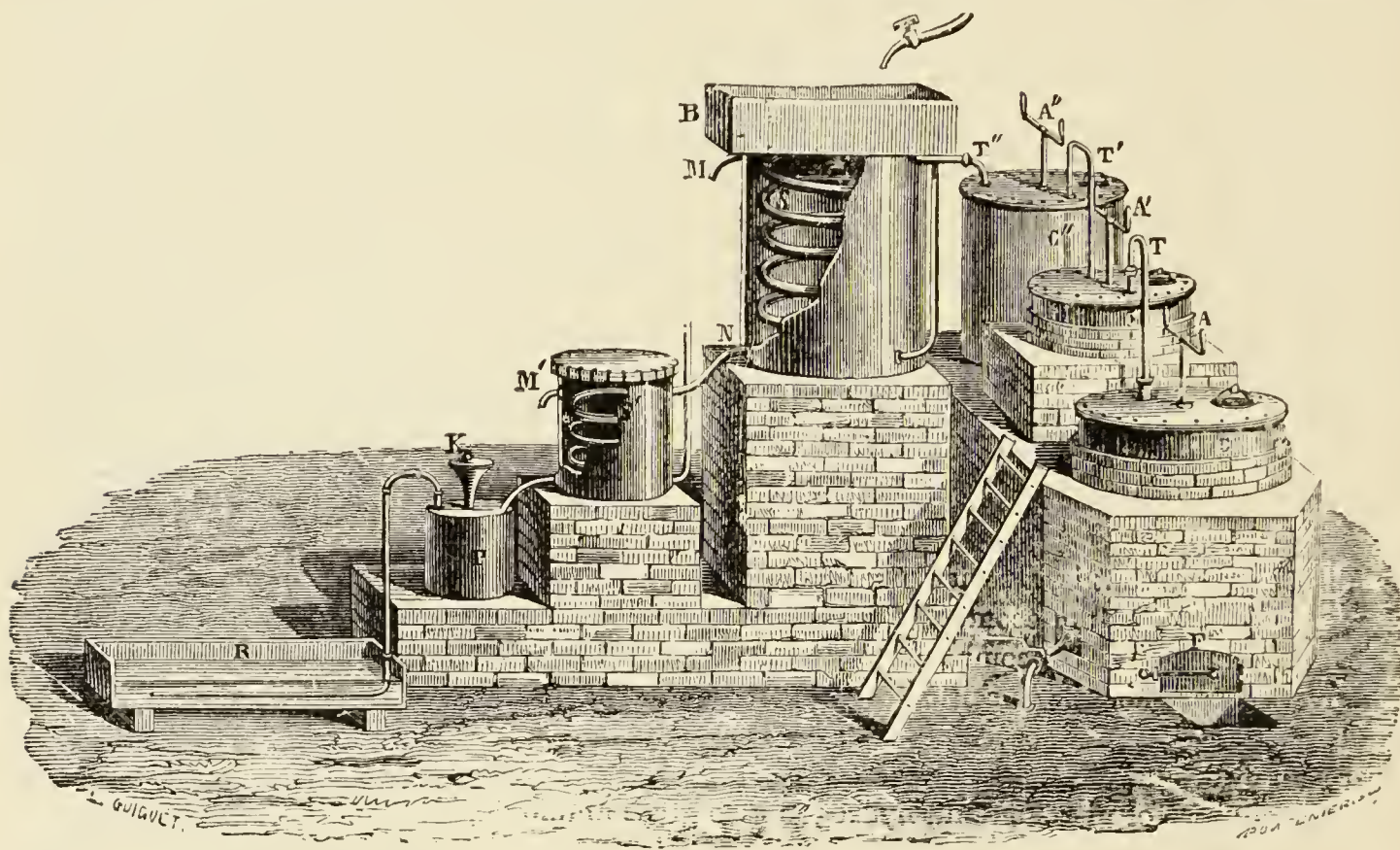


FIG. 49.—Method of abstracting ammonia, on a large scale, from ammonia water obtained at gas-works by the dry distillation of coal, or by the fermentation of urine, &c. This water is mixed with lime and poured into the boiler C'', and thence into C' and C consecutively. The last boiler is heated directly over a furnace, and hence no ammonia remains in solution after the liquid has been boiled in it. The liquid is therefore then thrown away. The ammonia vapour and steam pass from the boiler C, through the tube T, into the boiler C', and then into C'', so that in C' the solution becomes stronger than in C, and still stronger in C''. The boilers are furnished with stirrers A, A', and A'' to prevent the lime from settling. From C'' the ammonia and steam pass through the tube T'' into worm condensers surrounded with cold water, thence into the Woulfe's bottle P, where the solution of ammonia is collected, and finally the still uncondensed ammonia vapour is led into the flat vessel R, containing acid which absorbs the last traces of ammonia.

liquor obtained in the preparation of coal gas and coke (which contains ammonium salts, chiefly the carbonate in solution) is placed in a retort with lime and heated; the ammonia is then evolved together with steam.⁴ In the arts, only a small amount of ammonia is used in a free state, that is, in aqueous solution; the greater portion of it is converted into different salts having technical uses, especially

of the complex nitrogenous substances occurring in plants and animals. The ammonium salts employed in the arts are prepared by this method. The greater part of the ammonium salts are now prepared from the ammonia water obtained as a by-product in the dry distillation of coal in the manufacture of coke and illuminating gas.

⁴ The technical methods for the preparation of ammonia water, and for the extraction of ammonia from it, are to a certain extent explained in the figures accompanying the text.

sal-ammoniac, NH_4Cl , and ammonium sulphate, $(\text{NH}_4)_2\text{SO}_4$. They are saline substances which are formed on account of the capability of ammonia, NH_3 , of combining with all acids, HX , forming ammonium salts, NH_4X . Sal-ammoniac, NH_4Cl , is a compound of ammonia with hydrochloric acid. It is prepared by passing the vapours of ammonia and water, evolved, as above described, from ammoniacal liquor, into an aqueous solution of hydrochloric acid; on evaporating the solution, sal-ammoniac is obtained in the form of soluble crystals⁵ resembling common salt in appearance and properties. **Ammonia** may be very easily prepared from this **sal-ammoniac**, NH_4Cl , as from any other ammoniacal salt, by heating it with lime. Calcium hydroxide, CaH_2O_2 , being an alkali, takes up the acid forming calcium chloride and sets free the ammonia, according to the equation: $2\text{NH}_4\text{Cl} + \text{CaH}_2\text{O}_2 = 2\text{H}_2\text{O} + \text{CaCl}_2 + 2\text{NH}_3$. In this reaction the ammonia is evolved as a gas.⁶

It must be observed that all the complex nitrogenous substances of plants, animals, and soils are decomposed when heated with an excess of sulphuric acid, the whole of their nitrogen being converted into ammonium sulphate, from which it may be liberated by treatment with an excess of alkali. This reaction is so complete that it forms the basis of Kjeldahl's method for estimating the amount of nitrogen in its compounds.

Ammonia is a colourless **gas**, resembling, in its outward appearance, those with which we are already acquainted, but clearly distinguishable from any other gas by its very characteristic and pungent smell. It irritates the eyes, and it is positively impossible to inhale it. Animals die in it. Its density, referred to that of hydrogen, is 8.5; hence it is lighter than air. It belongs to the class of gases which are easily liquefied.⁷

⁵ Usually these crystals are sublimed by heating them in crucibles or pots, when the vapours of sal-ammoniac condense on the cold covers as a crust, in which form the salt is placed on the market.

⁶ In the laboratory ammonia may be prepared in a glass flask by mixing equal parts by weight of slaked lime and finely powdered sal-ammoniac, the neck of the flask being connected with an arrangement for drying the gas obtained. In this instance neither calcium chloride nor sulphuric acid can be used for drying the gas, since both these substances absorb ammonia, and therefore solid caustic potash, which is capable also of retaining the water, is employed. The gas-conducting tube leading from the desiccating apparatus is introduced into a mercury bath, if dry gaseous ammonia is required, because water cannot be employed in collecting ammonia gas. Ammonia was first obtained in this dry state by Priestley, and its composition was investigated by Berthollet at the end of the eighteenth century. Oxide of lead mixed with sal-ammoniac (Isambert) evolves ammonia with still greater ease than lime. The cause and process of the decomposition are almost the same: $2\text{PbO} + 2\text{NH}_4\text{Cl} = \text{Pb}_2\text{OCl}_2 + \text{H}_2\text{O} + 2\text{NH}_3$, lead oxychloride being (probably) formed.

⁷ This is evident from the fact that its absolute boiling-point lies at about $+130^\circ$ (Chap. II., note 29). It may therefore be liquefied by pressure alone at the ordinary, and

Faraday employed the following method for liquefying ammonia. Ammonia when passed over dry silver chloride, AgCl , is absorbed by it

even at much higher temperatures. The latent heat of evaporation of ammonia is about 300 units of heat; and hence liquid ammonia may be employed for the production of cold. Strong aqueous solutions of ammonia, which in parting with their ammonia act in a similar manner, are not infrequently employed for this purpose. Suppose a saturated solution of ammonia to be contained in a closed vessel furnished with a receiver. If the ammoniacal solution be heated, the ammonia, with a small quantity of water, will pass off from the solution, and in accumulating in the apparatus will produce a considerable pressure, and will therefore liquefy in the cooler portions of the apparatus. Hence liquid ammonia will be obtained in the receiver. The heating of the vessel containing the aqueous solution of ammonia is then stopped. After having been heated it contains only water, or a solution poor in ammonia. When once it begins to cool, the ammonia vapours commence dissolving in it, the space becomes rarefied, and a rapid vaporisation of the liquefied ammonia left in the receiver takes place. In evaporating in the receiver it will cause the temperature therein to fall considerably, and will itself pass into the aqueous solution. In the end, the same ammoniacal solution as was originally taken is re-

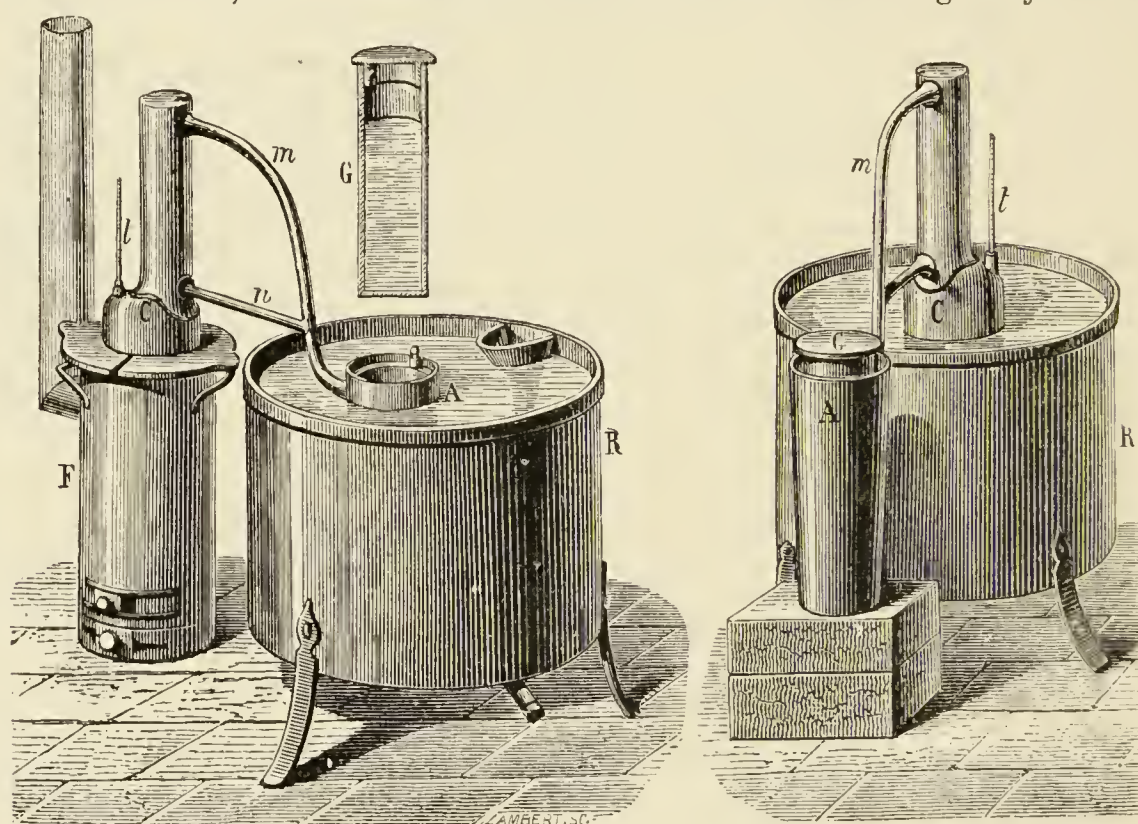


FIG. 50—Carré's apparatus. Described in text.

obtained. Thus, in this case, on heating one portion of the closed vessel, compression of the ammonia takes place, and on cooling, the liquid evaporates and so generates great cold. This is the principle of the simplest form of *Carré's ice-making machine*, shown in fig. 50. C is a vessel made of boiler plates into which the saturated solution of ammonia is poured; m is a tube conducting the ammonia vapour to the receiver A. All parts of the apparatus should be hermetically joined together, and should be able to withstand a pressure of ten atmospheres. The apparatus should be freed from air, which would otherwise hinder the liquefaction of the ammonia. The process is carried on as follows:—The apparatus is first so inclined that any liquid remaining in A may flow into C. The vessel C is then placed upon a stove F, and heated until the thermometer t indicates a temperature of 130°C . During this time the ammonia has been expelled from C, and has liquefied in A. In order to facilitate the liquefaction, the receiver A should be immersed in a tank of water R (see the left-hand drawing in fig. 50). When it may be supposed that the ammonia has been expelled, the fire is removed from under C, which in its turn is immersed in the tank of water R, as is represented in the right-hand drawing of

to a considerable extent, especially at low temperatures.⁸ The solid compound, $\text{AgCl}\cdot 3\text{NH}_3$, thus obtained is introduced into a thick bent tube (fig. 51), whose open end *c* is then fused up. The compound is then slightly heated at *a*, and the ammonia comes off, owing to the easy dissociation of the compound. The other end of the tube is immersed in a freezing mixture. The pressure of the gas coming off combined with the low temperature at one end of the tube, causes the ammonia evolved to condense into a liquid, in which form it collects at the cold end of the tube. If the heating be stopped, the silver chloride will again absorb the ammonia. In this manner one tube may serve for repeated experiments. Ammonia may always be liquefied by the ordinary methods—that is, by pumping dry ammonia gas into a refrigerated space. Liquefied ammonia is a colourless and very mobile liquid,⁹ whose specific gravity at 0° is 0.63 (E. Andr  eff). At the temperature given by a mixture of liquid carbonic anhydride and ether, liquid ammonia crystallises, and in this form its odour is feeble, because at so low a temperature its vapour pressure is very inconsiderable. The boiling-point (at 760 mm.) of liquid ammonia is about 34° , the melting-point about -78° , and the absolute (critical) boiling-point about $+130^\circ$.

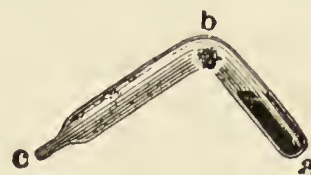


FIG. 51.—The liquefaction of ammonia in a thick bent glass tube. A compound of chloride of silver and ammonia is placed in the end *a*, and the end *c* is then sealed up.

Ammonia, containing, as it does, a large proportion of hydrogen, is fig. 50. The liquefied ammonia then evaporates, and passes over into the water in C. This causes the temperature of A to fall considerably. The substance to be refrigerated is placed in a vessel G, in the cylindrical space inside the receiver A. The heating and also the refrigeration are kept on for about half an hour, and with an apparatus of ordinary dimensions (containing about two litres of ammonia solution), five kilograms of ice are produced by the consumption of one kilogram of coal. In industrial works larger and more complicated types of Carr  's machines are employed.

⁸ Below 15° (according to Isambert), the compound $\text{AgCl}\cdot 3\text{NH}_3$ is formed, and above 20° the compound $2\text{AgCl}\cdot 3\text{NH}_3$. The pressure of the ammonia evolved from the latter substance is equal to the atmospheric pressure at 68° , whilst for $\text{AgCl}\cdot 3\text{NH}_3$ the same happens at about 20° ; hence, at higher temperatures, the pressure is greater than that of the atmosphere, whilst at lower temperatures the ammonia is absorbed and forms this compound. Consequently, all the phenomena of dissociation are here clearly to be observed. Joannis and Croisier (1894) made investigations with AgBr , AgI , AgCN , and AgNO_3 , and found that they all give definite compounds with NH_3 ; for instance, $\text{AgBr}\cdot 3\text{NH}_3$; $2\text{AgBr}\cdot 3\text{NH}_3$ and $\text{AgBr}\cdot 2\text{NH}_3$; they are all colourless solid substances which decompose under the atmospheric pressure at $+3.5^\circ$, $+34^\circ$, and $+51^\circ$ respectively.

⁹ The liquefaction of ammonia may be accomplished without increase of pressure by means of freezing mixtures producing temperatures below -35° . It may even take place in the severe frosts of a Russian winter. The application of liquid ammonia as a motive power for engines forms a problem which has to a certain extent been solved by the French engineer Tellier and others. Liquid ammonia resembles water in many respects; its specific heat is 1.02 (Ellean); the latent heat of evaporation at -30° is 330 cal. (pressure 1.15 atmosphere), at $0^\circ = 316$ (pressure 4.21 atmospheres), at $+30^\circ = 300$ cal. (pressure 11.62 atmospheres).

capable of combustion ; it does not, however, burn steadily, and sometimes not at all, in ordinary atmospheric air (the temperature not being sufficiently high). In pure oxygen it burns with a greenish-yellow flame,¹⁰ forming water, whilst the nitrogen set free gives partly oxygen compounds, that is, oxides of nitrogen, and partly escapes in an uncombined form. The decomposition of ammonia into hydrogen and nitrogen not only takes place at a red heat and under the action of electric sparks, but also under the influence of many oxidising substances ; for instance, by passing ammonia through a tube containing red-hot copper oxide. The water thus formed may be collected by substances absorbing it, and the nitrogen may be measured in the gaseous state, and thus the composition of ammonia determined. In this manner it is found that ammonia contains very nearly 3 parts by weight of hydrogen to 14 parts by weight of nitrogen ; whilst 3 vols. of hydrogen and 1 vol. of nitrogen form 2 vols of ammonia.¹¹

Ammonia is capable of combining with a number of substances, forming, like water, compounds of various degrees of stability. It is more **soluble** than any of the gases yet described, both in water and in many aqueous solutions. We have already seen, in the first chapter, that one volume of water, at the ordinary temperature, dissolves about 700 vols. of ammonia gas. If a piece of ice be placed in ammonia gas it melts and absorbs the gas with great rapidity. The great solubility of ammonia enables it to be kept ready for use in the form of an aqueous solution,¹² which is known commercially as **spirits of hartshorn**.

¹⁰ The combustion of ammonia in oxygen may be easily demonstrated by means of incandescent platinum. A small quantity of an aqueous solution of ammonia, containing about 20 per cent. of the gas, is poured into a wide-mouthed beaker of about one litre capacity. A gas-conducting tube about 10 mm. in diameter, and supplying oxygen, is immersed in the aqueous solution of ammonia. But before introducing the gas, an incandescent platinum spiral is placed in the beaker ; in the presence of the platinum the ammonia is oxidised and burns, whilst the platinum wire becomes still more incandescent. The solution of ammonia is heated and oxygen passed through the solution. The oxygen, as it bubbles off from the ammonia solution, carries with it a part of the ammonia, and this mixture explodes on coming into contact with the incandescent platinum. This is followed by a certain cooling effect owing to the combustion ceasing ; but after a short interval this is renewed, so that one feeble explosion follows another. During the period of oxidation without explosion, white vapours of ammonium nitrite and red-brown vapours of oxides of nitrogen make their appearance, while during the explosion there is complete combustion, and consequently water and nitrogen are formed.

¹¹ This may be verified by their densities. Nitrogen is 14 times denser than hydrogen, and ammonia, $8\frac{1}{2}$ times. If 3 volumes of hydrogen with 1 volume of nitrogen gave 4 volumes of ammonia, then these 4 volumes would weigh 17 times as much as 1 volume of hydrogen ; consequently 1 volume of ammonia would be $4\frac{1}{4}$ times heavier than the same volume of hydrogen. But if these 4 volumes only give 2 volumes of ammonia, the latter will be $8\frac{1}{2}$ times as dense as hydrogen, which is found to be actually the case.

¹² Aqueous solutions of ammonia are lighter than water, and at 15° (taking water at 4° as 10,000) their specific gravity, s , as dependent on p , the percentage amount (by weight)

Ammonia water is continually evolving ammoniacal vapour, and so has the characteristic smell of ammonia itself, and is therefore employed for making smelling salts. It is a very characteristic and important

of ammonia, is given by the expression: $s = 9,992 - 42.5p + 0.21p^2$; for instance, with 10 per cent., $s = 9,588$. If t represents the temperature between the limits of $+10^\circ$ and $+20^\circ$, then the expression $(15 - t)(1.5 + 0.14p)$ must be added to the above formula for the specific gravity. Solutions containing more than 24 per cent. of the gas have not been sufficiently investigated with respect to the variation of their specific gravity. It is, however, easy to obtain more concentrated solutions, and at 0° solutions approaching $\text{NH}_3, \text{H}_2\text{O}$ (48.6 per cent. NH_3) in their composition, and of sp. gr. 0.85, may be prepared. But such solutions give up much of their ammonia at the ordinary temperature, so that more than 24 per cent. of NH_3 is rarely contained in solution. Ammonia solutions containing a considerable amount of ammonia give at temperatures far below 0° (for instance, an 8 per cent. solution at -14° and the strongest solutions at -48°) ice-like crystals which seem to contain ammonia. The whole of the ammonia may be expelled from a solution by heating, even at a comparatively low temperature; hence on heating aqueous solutions containing ammonia, a very strong solution of ammonia is obtained in the distillate. Alcohol, ether, and many other liquids are also capable of dissolving

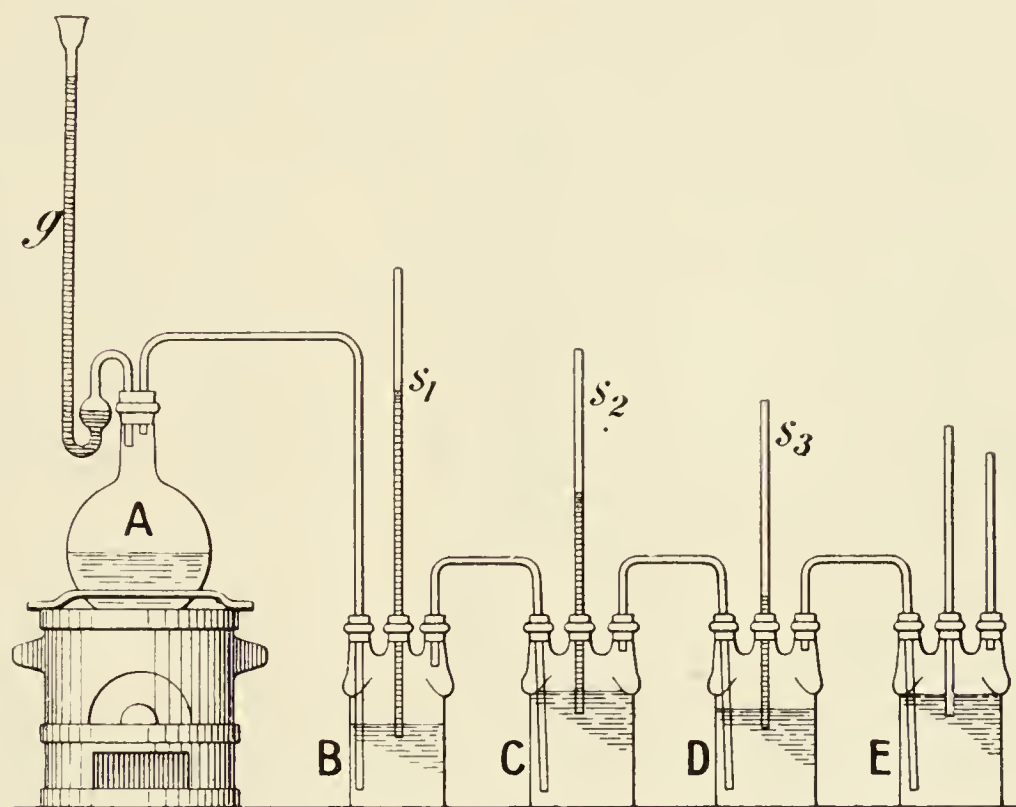


FIG. 52.—Apparatus for preparing solutions of ammonia.

ammonia. Solutions of ammonia, when exposed to the atmosphere, give off a part of their ammonia in accordance with the laws of the solutions of gases in liquids, which we have already considered. But the ammoniacal solutions at the same time absorb carbonic anhydride from the air, and ammonium carbonate remains in the solution.

Solutions of ammonia are required both for laboratory and factory operations, and have therefore to be frequently prepared. For this purpose the arrangement shown in fig. 52 is employed in the laboratory. In works the same arrangement is used, only on a larger scale (with earthenware or metallic vessels). The gas is prepared in a flask A, whence it is led through a series of Woulfe's bottles, B, C, D, E. The gas is dissolved in B, but the solution soon becomes saturated, and a purer (washed) ammonia passes over into the following vessels, in the last of which only a pure solution is obtained. The bent funnel tube G in the flask preserves the apparatus from the possibility both of the pressure of the gas evolved in it becoming too great (when the gas escapes through it into

fact that ammonia has an alkaline reaction, and colours litmus paper blue, just like caustic potash or lime; it is therefore sometimes called **caustic ammonia** (volatile alkali). Acids may be saturated by ammonia water or gas in exactly the same way as by any other alkali. In this process **ammonia combines directly with acids**, and this forms the most characteristic chemical reaction of this substance. If sulphuric, nitric, acetic, or any other acid is brought into contact with ammonia, it absorbs it, and in so doing evolves a large amount of heat and forms a compound having all the properties of a salt. Thus, for example, sulphuric acid, H_2SO_4 , in absorbing ammonia, forms (on evaporating the solution) one or both of two salts, according to the relative quantities of ammonia and acid. One salt is formed from $\text{NH}_3 + \text{H}_2\text{SO}_4$, and consequently has the composition NH_4SO_4 , and the other is formed from $2\text{NH}_3 + \text{H}_2\text{SO}_4$, and its composition is therefore $\text{N}_2\text{H}_6\text{SO}_4$. The former has an acid

the air), and also from the pressure accidentally falling too low (for instance, owing to a cooling effect, or from the reaction stopping). If this takes place, the air passes into the retort, otherwise the liquid from B would be drawn into A. The safety tubes s_1 , s_2 , &c.,

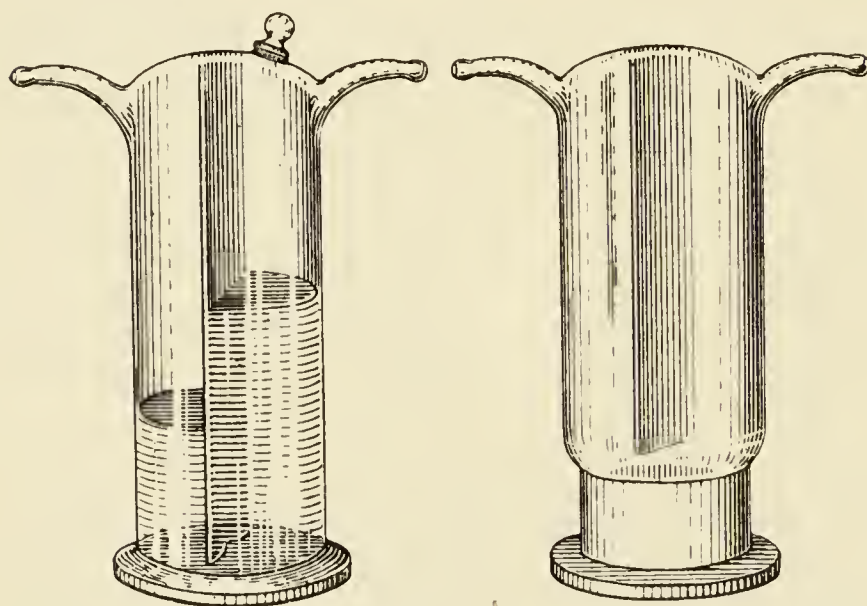


FIG. 53.—Tischenko's apparatus for washing or absorbing gases. In the form shown in the right-hand figure, solids such as fused calcium chloride, potash, &c. may be employed.

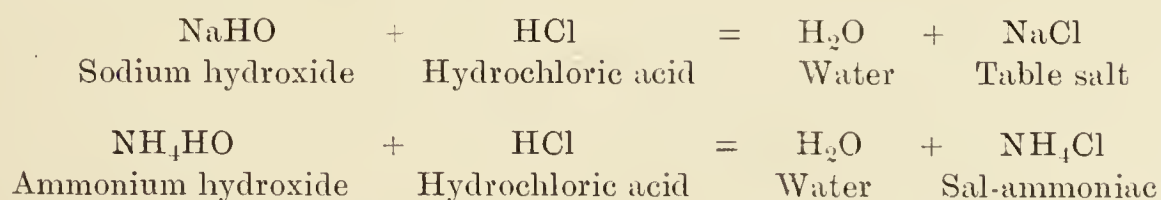
in each Woulfe's bottle, open at both ends and immersed in the liquid, serve for the same purpose. Without them, in case of an accidental stoppage in the evolution of so soluble a gas as ammonia, the solution would be sucked from one vessel to another; for instance, from E into D, &c. In order to see clearly the necessity for *safety tubes* in a gas apparatus, it must be remembered that the *gaseous pressure* in the interior of the arrangement must exceed the atmospheric pressure by the sum of the heights of the columns of liquid through which the gas has to pass.

Instead of setting up each time such a cumbersome and breakable apparatus as the above, various ready-made forms are now employed which greatly simplify the matter. Among such, Prof. Tischenko's apparatus, shown in fig. 53, is distinguished for its simplicity and regular action. It is composed of a glass jar furnished with a glass partition passing down the middle and having one or more holes at the bottom. A gas-conducting tube extends from the upper portion of each side of the jar, and the top is provided with a stoppered opening for pouring in the liquid used for washing the gas. If the liquid be introduced in such quantity as not quite to fill either half of the jar, but sufficient to cover the holes at the bottom of the partition, then the gas will be able to pass in either direction without forcing the liquid out of the jar. If, for instance, the pressure be greater on the right-hand side than the left, then the liquid will pass from the right to the left, and the gas will rise in bubbles through the column of liquid. If the pressure be reversed the same thing takes place in the opposite direction. A series of such jars may be advantageously used in the preparation of saturated solutions of ammonia.

reaction and the latter a neutral reaction, and they are called respectively acid ammonium sulphate (ammonium hydrogen sulphate) and normal ammonium sulphate or simply ammonium sulphate. Similar salts are formed by the action of all other acids; but certain of them are able to form normal ammonium salts only, whilst others give both acid and normal ammonium salts. This depends on the nature of the acid and not on the ammonia, as we shall afterwards see. Ammonium salts are very similar in appearance and in many of their properties to metallic salts; for instance, sodium chloride or table salt, NaCl , resembles sal-ammoniac, or ammonium chloride, NH_4Cl , not only in its outward appearance but even in crystalline form, in its property of giving precipitates with silver salts, in its solubility in water, and in its power of evolving hydrochloric acid when heated with sulphuric acid—in a word, a most perfect analogy is to be remarked in an entire series of reactions. An analogy in composition is seen if sal-ammoniac, NH_4Cl , be compared with table salt, NaCl ; or ammonium hydrogen sulphate, NH_4HSO_4 , with sodium hydrogen sulphate, NaHSO_4 ; or ammonium nitrate, NH_4NO_3 , with sodium nitrate, NaNO_3 , &c.¹³ It is seen, on comparing the above compounds, that the part which sodium takes in the sodium salts is played in ammonium salts by a group, NH_4 , which is called **ammonium**. If table salt be called ‘sodium chloride,’ then sal-ammoniac should be and is called ‘ammonium chloride.’

The hypothesis that ammoniacal salts correspond with a complex metal ammonium was enunciated by the famous Swedish chemist Berzelius, after a proposition put forward by Ampère. The analogy

¹³ The analogy between the ammonium and sodium salts might seem to be destroyed by the fact that the latter are formed from the alkali or oxide and an acid, with the separation of water, whilst the ammonium salts are directly formed from ammonia and an acid without the separation of water; but the analogy is restored if we compare soda to ammonia water, and liken caustic soda to a compound of ammonia with water. Then the very preparation of ammonium salts from such a hydrate of ammonia will completely resemble the preparation of sodium salts from soda. We may cite as an example the action of hydrochloric acid on both substances.



Just as in soda, so also in ammonia hydrate, the hydroxyl or aqueous radicle OH is replaced by chlorine. The analogy between NH_4 and Na and H is moreover exhibited by the fact that anhydrous peroxide of hydrogen directly absorbs ammonia gas (H_2O_2 is taken in the form of an ethereal solution) and forms a peroxide compound, NH_4HO_2 (cubical crystals insoluble in ether) like H_2O_2 or Na_2O_2 . Moissan in his researches on Weyl's compounds (see following note), for instance, NH_3Na , considers that free ammonium may be regarded as ammonia hydride, NH_3H , that is, as an analogue of these compounds.

between ammonium and metals is probable, owing to the fact that mercury is able to form an amalgam with ammonium similar to those which it forms with sodium and many other metals. The only difference between **ammonium amalgam** and sodium amalgam consists in the instability of the ammonium, which easily decomposes into ammonia and hydrogen.¹⁴ Ammonium amalgam may be prepared from sodium amalgam. If the latter be shaken up with a strong solution of sal-ammoniac the mercury swells up violently and loses its mobility whilst preserving its metallic appearance. In so doing the mercury dissolves ammonium—that is, the sodium in the mercury is replaced by the ammonium, which it replaces in the sal-ammoniac, forming sodium chloride, $\text{NH}_4\text{Cl} + \text{HgNa} = \text{NaCl} + \text{HgNH}_4$. Naturally the formation of ammonium amalgam does not absolutely prove the existence of ammonium itself in a separate state; but it shows the possibility of this substance existing, and its analogy with the metals,

¹⁴ By subjecting sodium to the action of ammonia at the ordinary temperature and under considerable pressures, Weyl (1864) obtained a liquid which was subsequently investigated by Joannis (1889), who confirmed Weyl's results. At 0° and the atmospheric pressure the composition of this substance is $\text{Na} + 5.3\text{NH}_3$. The removal (at 0°) of ammonia from the liquid gives a solid copper-red body having the composition NH_3Na . The determination of the molecular weight of this substance by the fall of the pressure of liquid ammonia gave the composition $\text{N}_2\text{H}_6\text{Na}_2$. It is therefore free ammonium in which one H is replaced by Na. Compounds with potassium, lithium, calcium, &c. proved to have analogous compositions. Dry NH_3 is absorbed by lithium at $+70^\circ$, forming a blue liquid, and it also gives similar liquids with sodium and potassium at -20° , whilst with metallic calcium at $+20^\circ$ it forms a solid compound, Ca_4NH_3 . When heated, all these compounds decompose into ammonia and the metal, or into an amide NH_2R and H_2 (Moissan, Chap. XIV., note 62). By the decomposition of NH_3Na at the ordinary temperature, Joannis (1891) obtained hydrogen and sodium amide, NH_2Na , in small colourless crystals soluble in water. The addition of liquid ammonia to metallic sodium and a saturated solution of sodium chloride gives $\text{NH}_2\text{Na}_2\text{Cl}$, that is, sal-ammoniac in which H_2 is replaced by Na_2 .

Ammonium amalgam was originally obtained in exactly the same way as sodium amalgam (Davy); namely, a piece of sal-ammoniac was taken and moistened with water (in order to render it a conductor of electricity). A cavity was made in it, into which mercury was poured, and it was laid on a sheet of platinum connected with the positive pole of a galvanic battery, the negative pole of which was put into connection with the mercury. On passing a current the mercury increased considerably in volume, and became plastic, while preserving its metallic appearance, just as would be the case were the sal-ammoniac replaced by a lump of a salt of sodium or of one of a number of other metals. Moissan (1901) prepared amalgams with the aid of liquid ammonia and low temperatures. The amalgam of sodium does not act upon liquid ammonia, but dry iodide of ammonium reacts, forming—without the evolution of gas—a liquid amalgam of ammonium which solidifies into a compact mass when cooled to -80° . If it be warmed (after washing and drying) it becomes liquid at -40° , and then effervesces and swells up owing to the formation of gases, which were found to contain hydrogen and ammonia, $2\text{NH}_3 + \text{H}_2$. All efforts to obtain the ammonium itself, for instance, by the reaction $2\text{NH}_3\text{Li} + \text{H}_2\text{S} = \text{Li}_2\text{S} + 2\text{NH}_4$ at low temperatures (to -70°) were unsuccessful, and only gave a mixture of NH_3 and H_2 .

because only metals dissolve in mercury.¹⁵ Ammonium amalgam crystallises in cubes, three times heavier than water; it is stable only in the cold, and particularly so at very low temperatures. It begins to decompose at the ordinary temperature, evolving ammonia and hydrogen in the proportion of two volumes of ammonia to one volume of hydrogen, $\text{NH}_4 = \text{NH}_3 + \text{H}$. Under the action of water, ammonium amalgam gives hydrogen and ammonia water, just as sodium amalgam gives hydrogen and sodium hydroxide; and therefore, in accordance with the ammonium theory, ammonia water or caustic ammonia must be looked on as containing ammonium hydroxide, NH_4OH ,¹⁶ just as an aqueous solution of caustic soda contains NaOH . The ammonium hydroxide, like ammonium itself, is an unstable substance, which readily dissociates and can only exist in a free state at low temperatures.¹⁷ Ordinary solutions of ammonia may be looked upon as the products of the dissociation of this hydroxide, inasmuch as $\text{NH}_4\text{OH} = \text{NH}_3 + \text{H}_2\text{O}$. In its chemical reactions caustic ammonia (and in general, solutions of NH_3 in water) is exactly similar to caustic soda, NaHO ; thus it neutralises acids, enters into double saline decompositions (for instance, a salt MX gives the reaction, $\text{NH}_4\text{OH} + \text{MX} = \text{NH}_4\text{X} + \text{MOH}$), &c., only with this difference, that this alkali can be entirely and readily volatilised.

All ammoniacal salts **decompose at a red heat** into ammonia and an acid, which, on cooling in contact with each other, recombine. If the acid be non-volatile, the ammoniacal salt, when heated, evolves the ammonia, leaving the non-volatile acid behind; if the acid be volatile, then, on heating, both the acid and ammonia volatilise together, and on cooling recombine into the salt which originally served for the formation of their vapours.¹⁸

¹⁵ We may mention, however, that under certain conditions hydrogen is also capable of forming an amalgam resembling the amalgam of ammonium. If an amalgam of zinc is shaken up with an aqueous solution of platinum chloride, without access of air, a spongy mass is formed which easily decomposes, with evolution of hydrogen.

¹⁶ We saw above (note 12) that the solubility of ammonia in water at low temperatures attains to the molecular ratio, $\text{NH}_3 + \text{H}_2\text{O}$, in which these substances are contained in caustic ammonia; and it may perhaps be possible, at exceedingly low temperatures, to obtain ammonium hydroxide, NH_4HO , in a solid form. Regarding solutions as dissociated definite compounds, we should see a confirmation of this view in the property shown by ammonia of being extremely soluble in water, and in so doing of approaching to the limit NH_4HO .

¹⁷ In confirmation of the truth of this conclusion we may cite the fact that there exist, in a free state and as comparatively stable compounds, a series of alkaline hydroxides, NR_4HO , which are perfectly analogous to ammonium hydroxide, and present a striking resemblance to it and to sodium hydroxide, with the only difference that the hydrogen in NH_4HO is replaced by complex groups, $\text{R} = \text{CH}_3$, C_2H_5 , &c., for instance $\text{N}(\text{CH}_3)_4\text{HO}$. Details will be found in works on organic chemistry.

¹⁸ The fact that ammoniacal salts are decomposed when ignited, and not simply sublimed, may be proved by a direct experiment with sal-ammoniac, NH_4Cl , which in a

Ammonia is capable of combining not only with acids, but also with many salts, as was seen from its forming definite compounds, $\text{AgCl}, 3\text{NH}_3$ and $2\text{AgCl}, 3\text{NH}_3$ (mentioned above), with silver chloride. Ammonia is absorbed with evolution of heat by various oxygen salts of the metals, and also by the chlorine, iodine, and bromine compounds of many metals. Certain of these compounds part with their ammonia when left exposed to the air, but others only do so at a red heat; many give up their ammonia when dissolved, whilst others dissolve without decomposition, and when their solutions are evaporated, separate unchanged. All these facts merely indicate that ammoniacal, like aqueous, compounds dissociate with greater or less facility.¹⁹ Certain metallic oxides also absorb ammonia and are dissolved by ammonia water. This is the case, for instance, with the oxides of zinc, nickel, copper, and many others, the majority of the compounds thus formed being unstable. The property of ammonia of combining with various oxides explains its action on certain metals, for instance, on copper in the presence of air.^{19a}

The similarity between the relations of ammonia and of water to salts and other substances is more especially marked in those cases in which the salt is capable of combining with both ammonia and water. Take, for example, copper sulphate, CuSO_4 , which, as we saw in Chapter I., gives with water blue crystals, $\text{CuSO}_4, 5\text{H}_2\text{O}$; but the anhydrous salt also absorbs dry ammonia in the same molecular proportions, forming a blue substance, $\text{CuSO}_4, 5\text{NH}_3$, and therefore the ammonia combining with salts may be termed **ammonia of crystallisation**.

Many **products** of direct or indirect **substitution** correspond to ammonia, its compounds with water and the ammonium salts. Certain

state of vapour is decomposed into ammonia, NH_3 , and hydrochloric acid, HCl , as will be explained in the following chapter. The readiness with which ammonium salts decompose is seen from the fact that a solution of ammonium oxalate is decomposed with evolution of ammonia even at -1° . Dilute solutions of ammonium salts, when boiled, give aqueous vapour having an alkaline reaction owing to the presence of free ammonia given off from the salt.

¹⁹ As we have seen in note 8, Isambert studied the dissociation of ammoniacal compounds, and showed that at low temperatures many salts are able to combine with a still greater amount of ammonia, which proves an entire analogy with hydrates; and as in this case it is easy to isolate the definite compounds, and as also the least possible pressure of ammonia is greater than that of water, the ammoniacal compounds present a great and peculiar interest, as a means of explaining the nature of aqueous solutions and as a confirmation of the hypothesis of the formation of definite compounds in them. For these reasons we shall frequently refer to these compounds in the further exposition of this work.

^{19a} Chap. V., note 2. This is the reason why copper vessels cannot be used for holding ammonia. Iron is not acted on by it. As zinc evolves hydrogen from ammonia (in aqueous solution) it may act like copper; but the affinity is small in this case, so that the oxygen affinity must also be taken into account. Copper alloys may be cleaned (the superficial coating of oxides removed) with a solution of ammonia.

of the elements, for instance, sodium, zinc, chlorine, &c., directly displace a portion of the hydrogen from NH_3 and take its place. The displaced hydrogen then appears either in the free state or combined with the simple body. If metallic sodium be heated in an atmosphere of dry ammonia it will displace a portion of the hydrogen in the ammonia and form sodium amide, NaNH_2 , according to the equation: $\text{NH}_3 + \text{Na} = \text{NaNH}_2 + \text{H}$. Chlorine acts in essentially the same way, forming ClNH_2 , but the hydrogen evolved, owing to its great affinity for chlorine, gives HCl , and in general the reaction is more complicated (see Chap. XI.), although fundamentally it is the same as in the case of sodium. Certain metallic compounds resembling ammonia in their composition and reactions, and in which the hydrogen is replaced by the metal, are formed directly by heating the metal in nitrogen. Thus lithium and magnesium readily absorb nitrogen when heated, forming nitrides, NLi_3 and N_2Mg_3 , which give ammonia with water (for instance, $\text{N}_2\text{Mg}_3 + 6\text{H}_2\text{O} = 3\text{MgH}_2\text{O}_2 + 2\text{NH}_3$). This shows that they, like sodium amide, are analogous to ammonia, and have the same composition and structure, with the difference that all the hydrogen is replaced by a metal, just as the metallic oxides correspond to water and may be regarded as products of substitution of the hydrogen in water by metals. But the hydrocarbon products of substitution of the hydrogen in ammonia present even greater interest. They have the composition NH_2R , NHR_2 , and NR_3 , where R is a hydrocarbon group (or residue), such as CH_3 , C_2H_5 , C_6H_5 , &c. These compounds, which are described fully in organic chemistry, are especially instructive because they preserve in themselves the faculty of ammonia for combining with acids and forming salts, and thus resemble ammonia completely in their chemical characters also. In nature such nitrogenous hydrocarbon derivatives of ammonia are met with in plants and animals, and are known as alkaloids owing to their capacity of combining with acids like ammonia; such, for instance, are quinine, nicotine, &c.²⁰

²⁰ The practical applications of ammonia are very varied. The use of ammonia as a stimulant, in the form of the so-called 'smelling salts' or of spirits of hartshorn, in cases of faintness, &c., is known to everyone. The volatile carbonate of ammonium, or a mixture of an ammonium salt with an alkali, is also employed for this purpose. Ammonia also produces a well-known stimulating effect when rubbed on the skin, for which reason it is sometimes employed for external applications. Thus, for instance, the well-known volatile salve is prepared from any liquid oil by shaking up with a solution of ammonia. A portion of the oil is thus transformed into a soapy substance. The solubility of greasy substances in ammonia, which proceeds from the formation both of emulsions and soaps, explains its use in extracting grease-spots. It is also employed as an external application for stings from insects and for poisonous snake-bites, and in general in medicine. It is also remarkable that in cases of drunkenness a few drops of ammonia in water taken internally rapidly renders a person sober. A large quantity of ammonia is used in dyeing, either for the solution of certain dyes—for example, carmine—or for

We shall now pass on to the consideration of the other compounds of nitrogen with hydrogen, and also of those with oxygen.

But in order to grasp the relation between ammonia and the other compounds of nitrogen it is necessary to recognise the general **law of substitution**, which is applicable to all cases of substitution between elements,^{20a} and to show therefore what may be the conditions of substitution between oxygen and hydrogen as component parts of water. The law of substitution may be deduced from mechanical principles, if the molecule be conceived as a system of elementary atoms occurring in a certain chemical and mechanical equilibrium. By likening the molecule to a system of bodies in a state of motion—for instance, to the sum total of the sun, planets, and satellites, existing in conditions of mobile equilibrium—we should expect the action of one part in this system to be equal and opposite to the other, according to Newton's third law of mechanics. Hence, given a molecule of a compound, for instance, H_2O , NH_3 , NaCl , HCl , &c., its two parts must, in a chemical sense, represent two things somewhat alike in force and properties, and therefore *every two parts into which a molecule of a compound may be divided are capable of replacing each other*.²¹ In order that the

changing the tints of others, or else for neutralising the action of acids. It is also employed in the manufacture of artificial pearls. For this purpose the small scales of a peculiar small fish are mixed with ammonia, and the liquid so obtained is blown into small hollow glass beads shaped like pearls.

In nature and the arts, however, ammonium salts, and not free ammonia, are most frequently employed. It is in this form that a portion of that **nitrogen** which is necessary for the formation of albuminous substances **is supplied to plants**. In this way a large quantity of ammonium sulphate is now employed as a fertilising substance. But the same effect may be produced by nitre or by animal refuse, which in decomposing gives ammonia. For this reason an ammoniacal (hydrogen) compound which may be introduced into the soil in the spring will be converted into a nitrate (oxygen salt) in the summer.

^{20a} When the element chlorine, as we shall afterwards more fully learn, replaces hydrogen, the reaction by which such an exchange is accomplished proceeds as a substitution, $\text{AH} + \text{Cl}_2 = \text{ACl} + \text{HCl}$, so that two substances, AH and chlorine, react on each other and two substances, ACl and HCl , are formed; and, further, two molecules react on each other, and two others are formed. Such reactions proceed very easily, but the substitution of one element, A , by another, X , does not always proceed with such ease, clearness or simplicity. The substitution between oxygen and hydrogen is very rarely accomplished by the direct action of the free elements, but the substitution between these elements, one for another, forms the most common case of oxidation or reduction. In speaking of the law of substitution, I have in view the substitution of the elements one by another, and not the direct reaction of substitution. The law of substitution determines the cycle of the combinations of a given element if a few of its compounds (for instance, the hydrogen compounds) be known. A development of the conceptions of the law of substitution may be found in my lecture given at the Royal Institution in London, 1889 (two lectures read in London. See 2nd edition of *Principles of Chemistry*).

²¹ It is evident from the essence of the matter that affinity must play a certain part in substitution, that is to say, that although chlorine, for instance, forms NaCl with

application of the law should become clear it is evident that among compounds the most stable should be chosen. We shall therefore take hydrochloric acid and water as the most stable compounds of hydrogen.^{21a} According to the above law of substitution, if the elements H and Cl are able to form a molecule, HCl, and a stable one, they are able to replace each other. And, indeed, we shall afterwards see (Chap. XI.) that in a number of instances substitution between hydrogen and chlorine can take place. Given RH, then RCl is possible, because HCl exists and is stable. The molecule of water, H₂O, may be divided in two ways, because it contains three atoms: into H and (HO) on the one hand, and into H₂ and O on the other. Consequently, being given RH, its substitution products will be R(HO) according to the first form, and R₂O according to the second; being given RH₂, its corresponding substitution products will be RH(OH), R(OH)₂, RO, (RH)₂O, &c. The group (OH) is the same **hydroxyl or aqueous radicle** which we have already mentioned in the third chapter as a component part of hydroxides and alkalies—for instance, Na(OH), Ca(OH)₂, &c. It is evident, judging from H(HO) and HCl, that (OH) can be substituted by Cl, because both are replaceable by H; and this is of common occurrence in chemistry, because metallic chlorides—for example, NaCl and NH₄Cl—correspond with hydroxides of the alkalis, Na(OH) or NH₄(OH). In hydrocarbons—for instance, C₂H₆—the hydrogen is replaceable by chlorine and by hydroxyl. Thus ordinary alcohol is C₂H₅(OH), in which one atom of H is replaced by (OH), that is, C₂H₅(OH). It is evident that the replacement of hydrogen by hydroxyl forms essentially the phenomenon of oxidation, because RH gives R(OH), or RHO. Hydrogen peroxide may

sodium, and therefore Cl can replace Na, yet this does not take place in every case. The law indicates the possibility of such a substitution taking place, and, what is still more important, it foretells the relative amounts of the substituting groups. Two atoms of hydrogen are replaced, judging from the composition of water, not by two atoms, but by one atom, of oxygen. The greater the complexity of the molecule the more difficult will it naturally be to obtain the products of substitution of all its subdivisions. It should further be remarked that in its above form the law of substitution simultaneously generalises the principles of such phenomena as metalepsis (see, in Chap. XI., the substitution of hydrogen by chlorine), oxidation, and homology (Chap. VIII.), which are as a rule (especially under the influence of the electrical and the dualistic conceptions) considered separately and independently of each other. The ordinary common instances of substitution of like by like are that quantities separately equal to some third are equal to each other; from which it is evident that if MX and RX exist then M can replace R, and *vice versa*.

^{21a} If hydrogen peroxide be taken as a starting-point, then still higher forms of oxidation than those corresponding with water should be looked for. They should possess the properties of hydrogen peroxide, especially that of parting with their oxygen with extreme ease (even by contact). Such compounds are known. Pernitric, persulphuric, and similar acids present these properties, as we shall see when describing them.

in this sense be regarded as water in which the hydrogen is replaced by hydroxyl; $\text{H}(\text{OH})$ gives $(\text{OH})_2$ or H_2O_2 . The other form of substitution—namely, that of O in the place of H_2 —is also a common chemical phenomenon. Thus alcohol, $\text{C}_2\text{H}_6\text{O}$, or $\text{C}_2\text{H}_5(\text{OH})$, when oxidising in the air, gives acetic acid, $\text{C}_2\text{H}_4\text{O}_2$, or $\text{C}_2\text{H}_3\text{O}(\text{OH})$, in which H_2 is replaced by O.

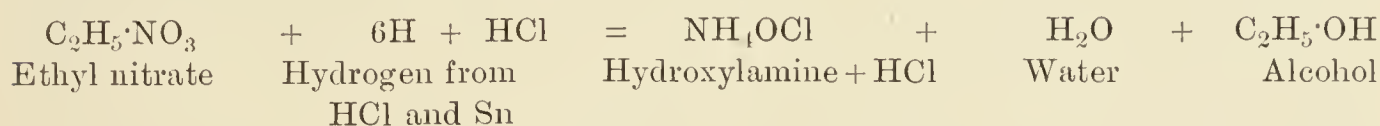
In the further course of this work we shall have frequent occasion to refer to the law of substitution for explaining many chemical phenomena and relations.

We shall now apply these conceptions to ammonia in order to see its relation to other compounds of nitrogen. It is evident that many substances should be obtainable from ammonia, NH_3 , or aqueous ammonia, $\text{NH}_4(\text{OH})$, by replacing their hydrogen by hydroxyl, or H_2 by oxygen. And such is the case. The extreme cases of substitution will be obtained on the one hand when we imagine the substitution of hydrogen in ammonia, NH_3 , by hydroxyl, so that $\text{NH}_2(\text{OH})$ is obtained, and on the other hand when we imagine that all the hydrogen in $\text{NH}_4(\text{OH})$ is replaced by oxygen, so that $\text{NO}_2(\text{OH})$ is formed. Both these possible extreme cases of the application of the law of substitution are evidently products of oxidation, for $\text{NH}_2(\text{OH}) = \text{NH}_3 + \text{O}$ and $2\text{NO}_2(\text{OH}) = 2\text{NH}_3 + 4\text{O}_2 + 2\text{H}_2\text{O}$, and they are both known as independent substances. The first, $\text{NH}_2(\text{OH})$, is called **hydroxylamine**, because substances containing the ammonia residue, NH_2 , are called amides or amines, and the residue itself amide, and the aqueous residue OH , as we already know, is called hydroxyl, and here these two are combined together. The second of the above substitution products, the highest oxidation compound, $\text{NO}_2(\text{OH})$, is nothing else but nitric acid, which corresponds to the anhydride, N_2O_5 , and salts NMO_3 . And as intermediate substitution products can be placed between these two extreme cases, we see that, starting from ammonia and its compound with water, we are enabled by the law of substitution to understand the relations of all the known compounds of nitrogen, hydrogen, and oxygen. It is simplest to start with caustic ammonia and substitution by hydroxyl.

The *first* product of this substitution will be $\text{NH}_3(\text{OH})_2 = \text{NH}_5\text{O}_2$. The separation of H_2O from it will give the above **hydroxylamine**, $\text{NH}_2(\text{OH})$. This substance was obtained as a salt, i.e., combined with an acid, in 1865 by Lossen as a product of the deoxidation (by the action of nascent hydrogen, SO_2 , and other reducing agents) of nitric acid. The salt formation is determined by the fact that hydroxylamine still contains a large proportion of hydrogen in combination with the nitrogen, so that the substance obtained is able, like ammonia, to

form salts with acids.²² But the formation of hydroxylamine, $\text{NH}_2(\text{OH}) = \text{NH}_3\text{O}$, indicates the possibility of the formation of two other compounds of nitrogen: N_2H_4 and NH , that is, of free amide $(\text{NH}_2)(\text{NH}_2) = \text{N}_2\text{H}_4$ and free imide NH (equivalent to $\text{NH}_3\text{O} - \text{H}_2\text{O}$), in which, as hydrogen compounds similar to ammonia, one would also expect to find a faculty for combining with acids. The possibility of the existence of free amide

²² The compound of hydroxylamine with hydrochloric acid has the composition $\text{NH}_2(\text{OH})\text{HCl} = \text{NH}_4\text{ClO}$, being, as it were, oxidised sal-ammoniac. It was prepared by Lossen in 1866 by the action of tin and hydrochloric acid in the presence of water on a substance called ethyl nitrate, the hydrogen liberated from the hydrochloric acid by the tin acting upon the elements of nitric acid—



Thus in this case the nitric acid is deoxidised, not directly into nitrogen, but into hydroxylamine. On mixing nitric acid with water and either sulphuric or hydrochloric acid, cooling the solution and subjecting it to the action of an electric current, using a mercury or amalgamated lead cathode, the nitric acid is almost completely reduced to hydroxylamine (Tafel, 1902). Hydroxylamine is also formed by passing nitric oxide, NO , into a mixture of tin and hydrochloric acid—that is, by the action of the hydrogen evolved on the nitric oxide, $\text{NO} + 3\text{H} + \text{HCl} = \text{NH}_4\text{OCl}$ —and in many other reactions. According to Lossen's method, a mixture of 30 parts of ethyl nitrate, 120 parts of tin, and 40 parts of a solution of hydrochloric acid of sp. gr. 1.06 is made, and after a certain time the reaction commences spontaneously. When the reaction has ceased the tin is separated by means of hydrogen sulphide and the solution evaporated, a large amount of sal-ammoniac being thus obtained (owing to the further action of hydrogen on the hydroxylamine compound, from which it takes up oxygen and forms water); a solution ultimately remains containing the hydroxylamine salt, which is dissolved in anhydrous alcohol and purified by the addition of platinum chloride, which precipitates any ammonium salt still remaining in the solution. After concentrating the alcoholic solution, the hydroxylamine hydrochloride separates in crystals. This substance melts at about 150° , and in so doing decomposes into nitrogen, hydrogen chloride, water, and sal-ammoniac. A sulphuric acid compound of hydroxylamine may be obtained by mixing a solution of the above salt with sulphuric acid; like the hydrochloride, it is soluble in water. Hydroxylamine, then, like ammonia itself, forms a series of salts in which one acid may be substituted for another. It might be expected that, by mixing a strong solution of a hydroxylamine salt with a solution of a caustic alkali, hydroxylamine itself would be liberated, just as an ammonium salt under these circumstances evolves ammonia; but the liberated hydroxylamine is immediately decomposed with the formation of nitrogen and ammonia (and probably nitrous oxide), $3\text{NH}_3\text{O} = \text{NH}_3 + 3\text{H}_2\text{O} + \text{N}_2$. Dilute solutions give the same reaction, although very slowly, but by decomposing a solution of the sulphate with barium hydroxide a certain amount of hydroxylamine is obtained in solution (it is partly decomposed). Like ammonia, hydroxylamine in aqueous solution precipitates basic hydrates, and it deoxidises the oxides of copper, silver, and other metals. Free hydroxylamine was obtained by Lobry de Bruyn (1891) and is a solid, colourless, crystalline substance (sp. gr. 1.935), without odour, and melting at $+33^\circ$. It is highly hygroscopic and readily distils under a low pressure (it is purified in this way), but decomposes with explosion when heated at the ordinary pressure. It is almost insoluble in ordinary solvents like chloroform, benzene, acetic ether, and carbon bisulphide. Its aqueous solutions, containing up to 60 per cent. (sp. gr. 1.15 at 20°), are tolerably stable, and may be kept for many weeks without undergoing any change. Lobry de Bruyn used the hydrochloric acid salt to prepare pure hydroxylamine. The salt was first

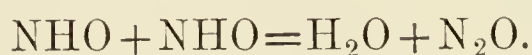
is in accordance with the law of substitution, because if ammonia be expressed as $(\text{NH}_2)\text{H}$, the group NH_2 should be able to replace hydrogen, and this exchange would result in the formation of amide $(\text{NH}_2)\text{NH}_2 = \text{N}_2\text{H}_4$. This substance was obtained by Curtius (1887), and was named **hydrazine**, N_2H_4 .^{22a} It forms a liquid boiling at about 113° , and

treated with sodium methylate, (CH_3NaO) , after which methyl alcohol was added to the mixture. The precipitated sodium chloride was separated from the solution by filtration. (The methyl alcohol is added to prevent the precipitated chloride of sodium from coating the insoluble hydrochloride of hydroxylamine.) Under the action of NaHO , hydroxylamine gives NH_3 and NHO_2 or N_2O , while it forms nitric acid (Kolotoff, 1893) under the action of oxidising agents. It is obtained in a great number of reactions; for instance, by the action of tin on dilute nitric acid and by the action of zinc on ethyl nitrate and dilute hydrochloric acid. The relation between hydroxylamine, $\text{NH}_2(\text{OH})$, and nitrous acid, $\text{NO}(\text{OH})$, which is so clear in the sense of the law of substitutions, becomes a reality in those cases in which reducing agents act on salts of nitrous acid. Thus Raschig (1888) proposed the following method for the preparation of hydroxylamine sulphate. A mixture of strong solutions of potassium nitrite, KNO_2 , and hydroxide, KHO , in molecular proportions, is prepared and cooled. An excess of sulphurous anhydride is then passed into the mixture and the solution boiled for a long time. A mixture of the sulphates of potassium and hydroxylamine is thus obtained: $\text{KNO}_2 + \text{KHO} + 2\text{SO}_2 + 2\text{H}_2\text{O} = \text{NH}_2(\text{OH})\cdot\text{H}_2\text{SO}_4 + \text{K}_2\text{SO}_4$, and these may be separated from each other by crystallisation.

^{22a} Free **amidogen** or **hydrazine**, N_2H_4 , or 2NH_2 , was prepared by Curtius (1887) by means of ethyl diazoacetate, or triazoacetic acid. Curtius and Jay (1889) showed that triazoacetic acid, $\text{CHN}_2\cdot\text{COOH}$ (the formula should be tripled), when heated with water or a mineral acid, gives (quantitatively) oxalic acid and amidogen (hydrazine), $\text{CHN}_2\cdot\text{COOH} + 2\text{H}_2\text{O} = \text{C}_2\text{O}_2(\text{OH})_2 + \text{N}_2\text{H}_4$ —i.e., expressed empirically, the oxygen of the water replaces the nitrogen of the azoacetic acid. The amidogen is thus obtained in the form of a salt. With acids, amidogen forms very stable salts of the two types $\text{N}_2\text{H}_4\cdot\text{HX}$ and $\text{N}_2\text{H}_4\cdot\text{H}_2\text{X}_2$; as, for example, with HCl , H_2SO_4 , &c. These salts are easily crystallised; in acid solutions they act as powerful reducing agents, evolving nitrogen; when ignited they are decomposed into ammoniacal salts, nitrogen, and hydrogen; with nitrites they evolve nitrogen. The sulphate $\text{N}_2\text{H}_4\cdot\text{H}_2\text{SO}_4$ is sparingly soluble in cold water (3 parts in 100 of water), but is very soluble in hot; its specific gravity is 1.378 and it fuses at 254° with decomposition. The hydrochloride $\text{N}_2\text{H}_4\cdot 2\text{HCl}$ crystallises in octahedra, is very soluble in water, but not in alcohol; it fuses at 198° , evolving hydrogen chloride and forming the salt $\text{N}_2\text{H}_4\cdot\text{HCl}$; when rapidly heated it decomposes with an explosion; with platinic chloride it immediately evolves nitrogen, forming platinous chloride. By the action of alkalis the salts $\text{N}_2\text{H}_4\cdot 2\text{HX}$ give **hydrate of amidogen**, $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$, which is a fuming liquid (specific gravity 1.03), solidifying at about 10° and boiling at 199° , almost without odour, and whose aqueous solution corrodes glass and indiarubber, has an alkaline taste and poisonous properties. With oxide of barium the hydrate gives anhydrous hydrazine as a liquid (sp. gr. 1.01) boiling at 113° (but it is best to distil it under a low pressure because it readily decomposes), and solidifying at about $+1^\circ$. The reducing properties of the hydrate are clearly seen from the fact that it reduces the metals platinum and silver from their solutions. With mercuric oxide it explodes. Iodic acid HIO_3 (and also its salts, even the insoluble barium salt BaI_2O_6) oxidises the salts of hydrazine at the ordinary temperature, and is entirely converted into hydriodic acid, with the evolution of free nitrogen (Ditte); for instance, $\text{BaI}_2\text{O}_6 + 3\text{N}_2\text{H}_4\cdot\text{H}_2\text{SO}_4 = 2\text{HI} + 2\text{H}_2\text{SO}_4 + \text{BaSO}_4 + 6\text{H}_2\text{O} + 3\text{N}_2$ (this reaction is so complete that the amount of barium may be determined by the volume of nitrogen evolved; it was proposed by Rigler as an analytical method). It reacts directly with the aldehydes RO , forming N_2R_2 and water; for example, with benzaldehydes it gives the very stable insoluble *benzalazine*, $(\text{C}_6\text{H}_5\text{CHN})_2$, of a yellow colour. We may add that hydrazine often forms double

capable of giving a stable hydrate $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$, which may be regarded as caustic ammonia, NH_4OH , in which H is replaced by NH_2 . This hydrate is distinctly alkaline. Hydrazine is also formed by reducing hyponitrous acid, $\text{N}_2(\text{OH})_2$, with ammonium sulphide, $\text{N}_2\text{H}_2\text{O}_2 + 3\text{H}_2 = \text{N}_2\text{H}_4 + 2\text{H}_2\text{O}$. We shall afterwards become acquainted with this acid, because, like amide, it forms one of the intermediate substances between ammonia and nitric acid, and so far such intermediary products have been almost exclusively obtained from more highly oxidised products by a method of reduction, and not by the oxidation of more highly hydrogenated compounds. The free amide NH (or maybe N_nH_n), equivalent to hydroxylamine less water, has not yet been obtained separately, and if it be at any time prepared, it will be as a substance which easily decomposes into nitrogen and hydrogen.²³

The *second* product of the substitution of hydrogen by hydroxyl, in caustic (aqueous) ammonia, $\text{NH}_2(\text{OH})_3 = \text{NH}_5\text{O}_3$, should by the abstraction of water give NH_3O_2 and NHO . This latter is hyponitrous acid, which appears, however, in the form of a polymeride, $\text{N}_2\text{H}_2\text{O}_2$, described further on. But as it still contains hydrogen and oxygen, it is to be expected that it should part with water, and give the nitrous oxide described later.



The *third* product of substitution, $\text{NH}(\text{HO})_4 = \text{NH}_5\text{O}_4$, when deprived

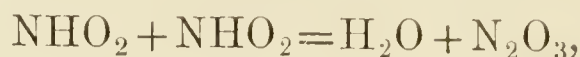
salts; for example, $\text{MgSO}_4\cdot\text{N}_2\text{H}_4\cdot\text{H}_2\text{SO}_4$ or $\text{KCl}\cdot\text{N}_2\text{H}_4\cdot\text{HCl}$, and that it is also formed by the action of nitrous acid upon aldehyde ammonia. The products of the substitution of the hydrogen in hydrazine by hydrocarbon groups R ($\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_6\text{H}_5$, &c.) were obtained before hydrazine itself; for example, NHRNH_2 , NR_2NH_2 , and $(\text{NRH})_2$.

The heat of formation of hydrated hydrazine, $-9\cdot5$ cals., from its elements was deduced from the heat of combustion, $+127\cdot7$ cals., determined by burning $\text{N}_2\text{H}_4\cdot\text{H}_2\text{SO}_4$ in a calorimetric bomb. Thus hydrazine is an endothermal compound: its passage into ammonia by combination with hydrogen is accompanied by the evolution of $51\cdot5$ cals. In the presence of an acid these figures become greater by $+14\cdot4$ cals. Hence the direct converse transformation of ammonia into hydrazine is impossible. As regards the passage of hydroxylamine into hydrazine, it would be accompanied in aqueous solution by an evolution of heat ($+21\cdot5$ cals.).

Amidogen must be regarded as a compound which stands in the same relation to ammonia as hydrogen peroxide to water. As was clearly to be expected, water, $\text{H}(\text{OH})$, gives, according to the law of substitution, $(\text{OH})(\text{OH})$ —that is, peroxide of hydrogen. So also ammonia, $\text{H}(\text{NH}_2)$, forms hydrazine, $(\text{NH}_2)(\text{NH}_2)$ —that is, the free radicle of ammonia, NH_2 , or amidogen. In the case of phosphorus a similar substance, as we shall afterwards see, has long been known under the name of liquid phosphoretted hydrogen, P_2H_4 .

²³ **Imide**, NH , has not been obtained in a free state, but its hydrochloric acid salt, NH_2HCl , has apparently been obtained (1890) by Maumené by igniting the double bichloride of platinum and ammonium chloride, $\text{PtCl}_2\cdot\text{NH}_4\text{Cl} = \text{Pt} + 2\text{HCl} + \text{NH}_2\text{HCl}$. It is soluble in water, and crystallises from its solution in hexagonal rhombic prisms. It gives a double salt with FeCl_3 of the composition $\text{FeCl}_3\cdot 3\text{NHHCl}$. The salt NH_2HCl is similar (isomeric) to the first possible product of the metalepsis of ammonia, NH_2Cl , although it can hardly resemble it in any of its properties.

of water, should yield nitrous acid (treated of later), NHO_2 , and its orthohydrate, $\text{N}(\text{OH})_3$, and by the total abstraction of the elements of water,



nitrous anhydride, N_2O_3 , which is also described in the following pages.

The *fourth* and last product of substitution, $\text{N}(\text{HO})_5$, less water, gives orthonitric acid, NH_3O_4 ,²⁴ and the most highly oxidised product of nitrogen, nitric acid, NHO_3 , and its anhydride, N_2O_5 :²⁵ $\text{NHO}_3 + \text{NHO}_3 = \text{H}_2\text{O} + \text{N}_2\text{O}_5$. And as it is supposed in the above equations that two molecules of hydrate are taken, it follows that intermediate oxides of nitrogen, N_2O_2 and N_2O_4 , or their polymerides, NO and NO_2 , may also be looked for. All these bodies are known and are described in what follows.

We shall, however, first show by two examples that in the first place the passage of ammonia into the oxygen compounds of nitrogen up to nitric acid, as well as the converse preparation of ammonia (and consequently of the intermediate compounds also) from nitric acid, are reactions which proceed directly and easily under many circumstances,²⁶

²⁴ Phosphorus (Chap. XIX.) gives the hydride PH_3 , corresponding with ammonia, NH_3 , and forms phosphorous acid, PH_3O_3 , which is analogous to nitrous acid, just as phosphoric acid is to nitric acid; but phosphoric (or, better, orthophosphoric) acid, PH_3O_4 , is capable of giving up water yielding pyro- and meta-phosphoric acids. The latter is equal to the ortho-acid minus water = PHO_3 , and therefore nitric acid, NHO_3 , is really meta-nitric acid. So also nitrous acid, HNO_2 , is meta-nitrous (anhydrous) acid, and thus the ortho-acid is $\text{NH}_3\text{O}_3 = \text{N}(\text{OH})_3$. Hence for nitric acid we should expect to find, besides the ordinary or meta-nitric acid, $\text{HNO}_3 (= \frac{1}{2}\text{N}_2\text{O}_5\text{H}_2\text{O})$, and ortho-nitric acid, $\text{H}_3\text{NO}_4 (= \frac{1}{2}\text{N}_2\text{O}_5, 3\text{H}_2\text{O})$, an intermediate pyro-nitric acid, $\text{N}_2\text{H}_4\text{O}_7$, corresponding with pyrophosphoric acid, $\text{P}_2\text{H}_4\text{O}_7$. We shall see (for instance, in Chap. XVI., note 21) that in nitric acid there is indeed an inclination of the ordinary salts (of the meta-acid) MNO_3 , to combine with bases M_2O , and to approximate to the composition of ortho-compounds which are equivalent to the meta-compound plus a base ($\text{MNO}_3 + \text{M}_2\text{O} = \text{M}_3\text{NO}_4$).

²⁵ Nitric acid corresponds with the anhydride N_2O_5 , which will afterwards be described, and which must be regarded as the highest saline oxide of nitrogen, just as is Na_2O (and the hydroxide NaHO) in the case of sodium, although sodium forms a peroxide, possessing the property of parting with its oxygen with the same ease as hydrogen peroxide, if not on heating, at all events in reactions—for instance, with acids. So also nitric acid has its corresponding peroxide, which may be called **pernitric acid**. Its composition is not well known, but is probably NHO_4 , so that its corresponding anhydride would be N_2O_7 . It is formed by the action of a silent discharge on a mixture of nitrogen and oxygen, a portion of its oxygen being hence similar to that in ozone. The instability of this substance (obtained by Hautefeuille, Chappuis, and Berthelot), which readily splits up with formation of nitric peroxide, and its resemblance to persulphuric acid, which we shall afterwards describe, will permit our passing over the consideration of the little that is further known concerning it.

²⁶ In reality it appears up to the present that the process of oxidation leads to the formation of nitric and nitrous acids, but not to the formation of the intermediate hydrogen compounds which so far have only been obtained by a method of reduction from higher degrees of oxidation. The action of a galvanic current on solutions of nitric acid, in the

and in the second place that the above general principle of substitution gives the possibility of understanding many, at first sight, unexpected and complex relations and transformations, such as the preparation of hydrazoic acid, HN_3 . In nature the matter is complicated by a number of influences and circumstances, but in the law the relations are presented in their simplest aspect.

It is easy to prove the possibility of the oxidation of ammonia into nitric acid by passing a mixture of ammonia and air over heated spongy platinum. This causes the oxidation of the ammonia, giving nitric acid, which partially combines with the excess of ammonia.

The converse transformation of nitric acid into ammonia is effected by the action of hydrogen at the moment of its evolution.²⁷ Thus metallic aluminium, evolving hydrogen from a solution of caustic soda, is able to completely convert nitric acid added to the mixture (as a salt, because the alkali gives a salt with the nitric acid) into ammonia, $\text{NHO}_3 + 8\text{H} = \text{NH}_3 + 3\text{H}_2\text{O}$. And as, judging from what was said above,

ammonia and nitric acid are the extreme compounds of nitrogen with hydrogen and oxygen, and all the other compounds of these elements may be regarded as intermediate compounds, so the passage of NH_3 to HNO_3 , and the reverse, clearly show that all the hydrogen and oxygen

presence of H_2SO_4 or HCl at the cathode, especially if the latter consist of mercury or an amalgamated metal, leads entirely to the formation of the hydroxylamine salt (Tafel, 1902); but as a rule reduction leads to the formation of ammonia, especially if the cathode be of copper.

²⁷ The formation of ammonia is observed in many cases of oxidation by means of nitric acid. This substance is even formed in the action of nitric acid on tin, especially if dilute acid be employed in the cold. A still more considerable amount of ammonia is obtained if, in the action of nitric acid, there are conditions directly tending to the evolution of hydrogen, which then reduces the acid to ammonia; for instance, in the action of zinc on a mixture of nitric and sulphuric acids. But hydrogen gas itself can in presence of platinum and by the aid of heat convert the oxide of nitrogen, for instance, NO , into ammonia:

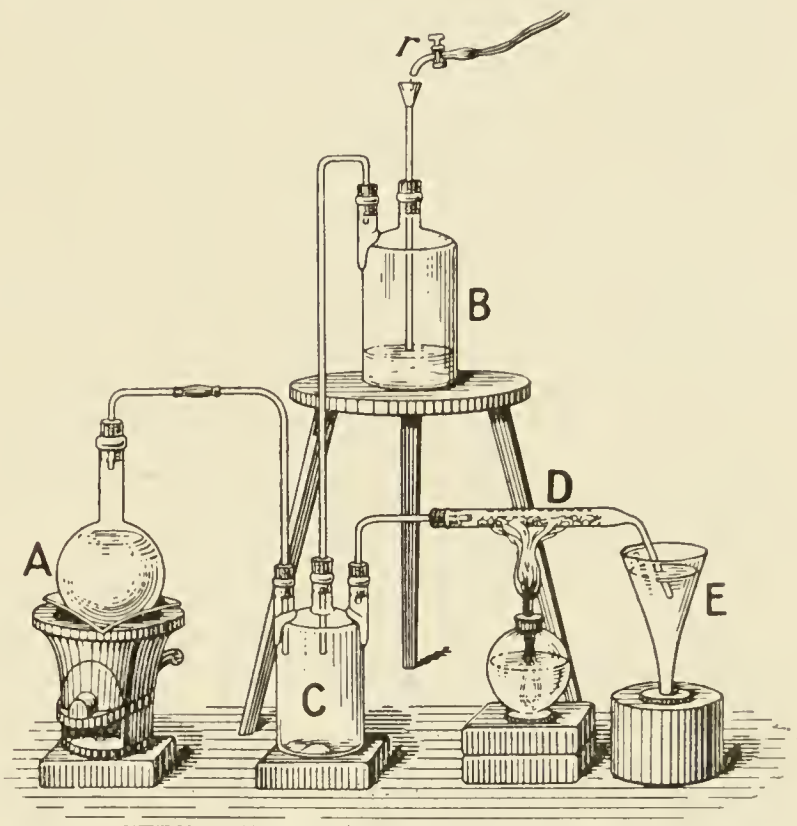
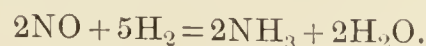


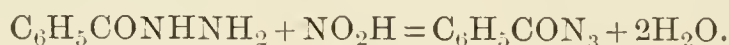
FIG. 54.—Conversion of ammonia into nitric acid. Air is driven out of the bottle B (by the stream of water from *r*) into C, where it mixes with the ammonia evolved from an aqueous solution in A. The mixed gases pass from C through the heated tube D containing spongy platinum. The nitric acid formed is collected in water in the vessel E.

compounds of nitrogen form one natural series. This sequence of compounds becomes particularly distinct when considered under the light of the law of substitutions.

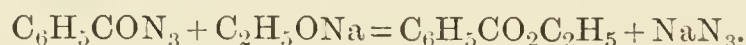
The same law gives the possibility of foreseeing the relations of trinitride of hydrogen, HN_3 , to the members of this series.

In 1890, Curtius, in Germany, obtained this substance as a very volatile (at $+37^\circ$), soluble, and very explosive liquid having the distinctive properties of an acid, dissolving zinc, aluminium, &c., with the evolution of hydrogen, and giving, like hydrochloric acid, salts; for example, a sodium salt, NaN_3 ; an ammonium salt, $\text{NH}_4\text{N}_3 = \text{N}_4\text{H}_4$; a barium salt, $\text{Ba}(\text{N}_3)_2$, &c. He therefore named it **hydrazoic acid**, HN_3 .^{27a} The extraordinary composition of the compound (ammonia,

^{27a} Curtius started with benzoylhydrazine, $\text{C}_6\text{H}_5\text{CONHNH}_2$ (hydrazine; see note 20a) (this substance is obtained by the action of hydrated hydrazine on the compound ether of benzoic acid). Benzoylhydrazine, under the action of nitrous acid, gives benzoylazoimide and water:



Benzoylazoimide when treated with sodium alcoholate gives the sodium salt of hydrazoic acid:



The addition of ether to the resultant solution precipitates the NaN_3 , and this salt, when treated with sulphuric acid, gives gaseous hydrazoic acid, HN_3 . It has an acrid smell, and is easily soluble in water. The aqueous solution exhibits a strongly acid reaction and dissolves metals, giving the corresponding salts. With hydrazoic acid, gaseous ammonia forms a white cloud, consisting of the ammonium salt, NH_4N_3 , which separates out from an alcoholic solution in the form of white lustrous scales. The salts of hydrazoic acid are obtained by reactions of substitution with the sodium or ammonium salts. In this manner Curtius obtained and studied the salts of silver (AgN_3), lead (PbN_6), and barium (BaN_6). With hydrazine, N_2H_4 , hydrazoic acid forms saline compounds in the composition of which there are one or two molecules of N_3H per one of hydrazine; e.g., N_5H_5 and N_8H_6 . The first, which was obtained in an almost pure form, crystallises from an aqueous solution in dense, volatile, lustrous prisms (up to 1 in. long), melting at 50° , and deliquescing in the air; from a solution in boiling alcohol it separates out in bright crystalline plates. This salt, N_5H_5 , has the same empirical composition, N_4H_4 , as imide, but its molecular weight and structure are different. Curtius also obtained (1893) hydrazoic acid by passing the vapour of N_2O_3 (evolved by the action of HNO_3 on As_2O_3) into a solution of hydrazine, N_2H_4 . Similarly Angeli, by acting upon a saturated solution of silver nitrite with a strong solution of hydrazine, obtained the explosive, AgN_3 , in the form of a precipitate, and this reaction, which is based upon the equation: $\text{N}_2\text{H}_4 + \text{NHO}_2 = \text{HN}_3 + 2\text{H}_2\text{O}$, proceeds so easily that it forms an experiment for the lecture table. The amide of potassium, NH_2K (obtained by the action of dry NH_3 on heated potassium), gives the potassium salt when acted upon by nitrous oxide, $\text{NH}_2\text{K} + \text{N}_2\text{O} = \text{N}_3\text{K} + \text{H}_2\text{O}$. This is the most convenient method for obtaining the potassium salt of hydrazoic acid, and therefore the acid itself. A thermal investigation of hydrazoic acid by Berthelot and Matignon gave for the heat of solution of the ammonium salt, $\text{N}_3\text{H}_4\text{N}_3$ (1 gram. in 100 parts of water) the value -708 cals. and for the heat of neutralisation by barium hydrate $+10.0$ cals. and by ammonia $+8.2$ cals. The heat of combustion of N_4H_4 ($+163.8$ cals. at a constant vol.) gives the heat of formation of the salt N_4H_4 (solid) as -25.3 cals. and (solution) -32.3 cals.; this explains the explosive nature of this compound. In its heat of forma-

NH_3 , contains one N atom and three H atoms ; in HN_3 , on the contrary, there are three N atoms and one H atom), the ready decomposition of its salts with explosion, and above all its distinctly acid character (an aqueous solution shows a strong acid reaction to litmus), not only indicated the importance of this unexpected discovery, but at first gave rise to some perplexity as to the nature of the substance obtained, for the relations in which HN_3 stood to other simple compounds of nitrogen which had long been known was not at all evident, and the scientific spirit requires that there should be a distinct bond between every innovation, every fresh discovery, and that which is already firmly established and known ; for upon this basis is founded that apparently paradoxical union in science of a conservative stability with an irresistible and never-ceasing improvement. This missing connection between the newly discovered hydrazoic acid, HN_3 , and the long known ammonia, NH_3 , and nitric acid, HNO_3 , may be found in the law of substitution, starting from the well-known properties and composition of nitric acid and ammonia, as I mentioned in the 'Journal of the Russian Physico-Chemical Society' (1890). The essence of the matter lies in the fact that to the hydrate of ammonium, or caustic ammonia, NH_4OH , there should correspond, according to the law of substitution, an ortho-nitric acid, $\text{H}_3\text{NO}_4 = \text{NO}(\text{OH})_3$, which equals $\text{NH}_4(\text{OH})$ with the substitution in it of (a) two atoms of hydrogen by oxygen ($\text{O}-\text{H}_2$) and (b) two atoms of hydrogen by the aqueous radicle ($\text{H}-\text{OH}$). The analogue of nitric acid, phosphoric acid, gives corresponding ortho- and meta-acids, PH_3O_4 and PHO_3 , with great ease, as we shall afterwards see (Chap. XIX.). The existence of an ortho-nitric acid, NH_3O_4 , is to be expected also from other analogies (Chapter XV.). Ordinary or meta-nitric acid is merely this ortho-nitric acid minus water. To ortho-nitric acid there should correspond the ammoniacal salts : mono-substituted, $\text{H}_2\text{NH}_4\text{NO}_4$; bi-substituted, $\text{H}(\text{NH}_4)_2\text{NO}_4$; and tri-substituted, $(\text{NH}_4)_3\text{NO}_4$. These salts, containing as they do hydrogen and oxygen, like many similar ammoniacal salts (see, for instance, Chapter IX.—Cyanides), are able to part with them in the form of water. Then from the first salt we have : $\text{H}_2\text{NH}_4\text{NO}_4 - 4\text{H}_2\text{O} = \text{N}_2\text{O}$ —nitrous oxide, and from the second, $\text{H}(\text{NH}_4)_2\text{NO}_4 - 4\text{H}_2\text{O} = \text{HN}_3$ —hydronitrous acid, and from the third, $(\text{NH}_4)_3\text{NO}_4 - 4\text{H}_2\text{O} = \text{N}_4\text{H}_4$ —the ammonium salt of the same acid. The composition of HN_3 should be thus understood, whilst its acid properties are explained by the fact that the water ($4\text{H}_2\text{O}$) from

tion from its elements, $\text{N}_3\text{H} = -62.6$ cals., this compound differs from all the hydrogen compounds of nitrogen in having a maximum absorption of heat, which explains its instability.

$\text{H}(\text{NH}_4)_2\text{NO}_4$ is formed at the expense of the hydrogen of the ammonium and the oxygen of the nitric acid, so that there remains the hydrogen of nitric acid, which may be replaced by metals and so give salts. Moreover, nitrogen undoubtedly belongs to the category of metalloids which give acids, like S, Cl, C, P, and therefore, under the influence of three of its atoms, one atom of hydrogen acquires those properties which it has in acids, just as in HCN (hydrocyanic acid) the hydrogen has received these properties under the influence of the carbon and nitrogen (and HN_3 may be regarded as HCN, where C has been replaced by N_2). Moreover, besides explaining the composition and acid properties of HN_3 , the above method gives the possibility of foretelling the closeness of the bond between hydrazoic acid and nitrous oxide, for $\text{N}_2\text{O} + \text{NH}_3 = \text{HN}_3 + \text{H}_2\text{O}$. This reaction, which was foreseen from the above considerations, was accomplished by Wislicenus (1892), who synthesised the sodium salt by taking the amide of sodium, NH_2Na (obtained by heating Na in a current of NH_3), and acting upon it (when heated) with nitrous oxide, N_2O , the reaction being: $2\text{NH}_2\text{Na} + \text{N}_2\text{O} = \text{NaN}_3 + \text{NaHO} + \text{NH}_3$. The resultant salt, NaN_3 , gives hydrazoic acid when acted upon by sulphuric acid, $\text{NaN}_3 + \text{H}_2\text{SO}_4 = \text{NaHSO}_4 + \text{HN}_3$. The latter gives, with the corresponding solutions of their salts, the insoluble (and readily explosive) salts of silver, AgN_3 (insoluble, like AgCl or AgCN), and lead, $\text{Pb}(\text{N}_3)_2$.

Thus the law of substitution in the above form renders it possible to connect the various compounds of nitrogen with hydrogen and oxygen by a more intimate bond.

The compounds of nitrogen with oxygen also present an excellent example of the law of multiple proportions, because they contain, for every 14 parts by weight of nitrogen, 8, 16, 24, 32, and 40 parts by weight respectively of oxygen. The compositions of these compounds are as follows:—

N_2O , nitrous oxide; hydrate NHO .

N_2O_2 , nitric oxide, NO .

N_2O_3 , nitrous anhydride; hydrate NHO_2 .

N_2O_4 , peroxide of nitrogen, NO_2 .

N_2O_5 , nitric anhydride; hydrate NHO_3 .

Of these compounds,²⁸ nitrous and nitric oxides, peroxide of nitrogen, and nitric acid, NHO_3 are characterised as being the most stable. *The lower oxides, when coming into contact with the higher, may give the intermediate forms, for instance, NO and NO_2 form N_2O_3 ; and the*

²⁸ According to the thermochemical determinations of Favre, Thomsen, and more especially of Berthelot, it follows that, in the formation of quantities of the oxides of nitrogen expressed by their formulæ, if gaseous nitrogen and oxygen be taken as

intermediate oxides may, in splitting up, give a higher and lower oxide, e.g., N_2O_4 gives N_2O_3 and N_2O , or, in the presence of water, their hydrates.

We have already seen that, under certain conditions, nitrogen combines with oxygen, and we know also that ammonia may be oxidised. In these cases various oxidation products of nitrogen are formed, but in the presence of water and an excess of oxygen they always give nitric acid. Nitric acid, as corresponding with the highest oxide, is able, on deoxidation, to give the lower oxides; it is the only nitrogen acid whose salts occur somewhat widely distributed in nature, and it has many technical uses, for which reason we shall begin with it.

Nitric acid, NHO_3 , is likewise known as aqua fortis. In a free state it is only met with in small quantities in nature, in the air and in rain-water after storms; but even in the atmosphere nitric acid does not long remain free, but combines with ammonia, traces of which are always found in air. On falling on the soil and into running water, &c., the nitric acid comes everywhere into contact with bases (or their salts), which readily act on it, so that it is converted into the nitrates of these bases. Hence nitric acid is always met with in nature in the form of salts. The soluble salts of nitric acid are called **nitres**. This name is derived from the Latin *sal nitri*. The potassium salt, KNO_3 , is common or prismatic nitre, and the sodium salt, $NaNO_3$, Chili salt-petre, or cubic nitre. Nitres are formed in the soil when a nitrogenous substance is slowly oxidised, in the presence of an alkali, by means of the oxygen of the atmosphere. In nature there are very frequent

the starting-points, and if the compounds formed be also gaseous, the following amounts of heat, expressed in thousands of heat units, are *absorbed* (hence a minus sign):—

N_2O	N_2O_2	N_2O_3	N_2O_4	N_2O_5
−21	−43	−22	−5	−1
−22	+21	+17	+4	

The differences are given in the lower line. For example, if N_2 , or 28 grams of nitrogen, combine with O—that is, with 16 grams of oxygen—21,000 units of heat will be absorbed, that is, sufficient heat to raise 21,000 grams of water through 1° . Naturally, direct observations are impossible in this case; but if charcoal, phosphorus, or similar substances are burned both in nitrous oxide and in oxygen, and the heat evolved observed in both cases, then the difference (more heat will be evolved in burning in nitrous oxide) gives the figures required. If N_2O_2 , by combining with O_2 , gives N_2O_4 , then, as is seen from the table, heat should be *developed* to the extent of 38,000 units, i.e., $NO + O = 19,000$ units of heat. The differences given in the table show that the maximum absorption of heat corresponds with nitric oxide, from which the higher oxides are formed with evolution of heat. If liquid nitric acid, NHO_3 , is to be decomposed into $N + O_3 + H$, 41,000 heat units will be required; that is, an evolution of heat takes place in its formation from the gases. It should be observed that the formation of ammonia, NH_3 , from the gases $N + H_3$ evolves 12·2 thousand heat units, so that free nitrogen has a greater tendency to combine with hydrogen than with oxygen.

instances of such oxidation. For this reason certain soils and rubbish heaps—for instance, lime rubbish (in the presence of a base—lime)—contain a more or less considerable amount of nitre. One of these nitres—sodium nitrate—is extracted from the earth in large quantities in Chili, where it was probably formed by the oxidation of animal refuse. This kind of nitre is employed in practice for the manufacture of nitric acid and the other oxygen compounds of nitrogen. Nitric acid is obtained from **Chili saltpetre** *by heating* it with **sulphuric acid**. The hydrogen of the sulphuric acid replaces the sodium in the nitre. The sulphuric acid then forms either an acid salt, NaHSO_4 , or a normal salt, Na_2SO_4 , whilst nitric acid is formed from the nitre and volatilised. The decomposition is expressed by the equation: (1) $\text{NaNO}_3 + \text{H}_2\text{SO}_4 = \text{HNO}_3 + \text{NaHSO}_4$, if the acid salt is formed, or by (2) $2\text{NaNO}_3 + \text{H}_2\text{SO}_4 = \text{Na}_2\text{SO}_4 + 2\text{HNO}_3$, if the normal sodium sulphate is formed. With an excess of sulphuric acid, at a moderate heat (up to 200°), and at the commencement of the reaction, the decomposition proceeds according to the first equation; and on further heating (to 230°) with a sufficient amount of nitre, according to the second, because the acid salt NaHSO_4 itself acts like an acid (its hydrogen being replaceable as in acids), according to the equation: $\text{NaNO}_3 + \text{NaHSO}_4 = \text{Na}_2\text{SO}_4 + \text{HNO}_3$.

The sulphuric acid, as it is said, here displaces the nitric acid from its compound with the base.²⁹ Thus, in the reaction of sulphuric acid on nitre there is formed a non-volatile salt of sulphuric acid, which remains together with an excess of this acid in the distilling apparatus,

²⁹ This often gives rise to the supposition that sulphuric acid possesses a considerable degree of affinity or energy compared with that of nitric acid, but we shall afterwards see that the conception of the relative degree of affinity of acids and bases is, in many cases, exceedingly inaccurate and need not be accepted so long as it is possible to explain the observed phenomena without admitting any supposition whatsoever of the degree of the force of affinity, because the latter cannot be measured. The action of sulphuric acid upon nitre may be explained by the simple fact that the resultant nitric acid is volatile. The nitric acid is the only one of all the substances partaking in the reaction which is able to pass into vapour, the others being non-volatile, or, more strictly speaking, exceedingly difficultly volatile substances. Let us imagine that the sulphuric acid is only able to set free a small quantity of nitric acid from its salt, and this will suffice to explain the decomposition of the whole of the nitre by the sulphuric acid, because when the nitric acid is separated it is formed into vapour on heating, and passes away from the sphere of action of the remaining substances; then the free sulphuric acid will liberate a further small quantity of nitric acid, and so on until it drives off the entire quantity. It is evident from this explanation that it is essential that the sulphuric acid should be in excess (although not greatly) throughout the reaction; according to the equation expressing the reaction, 98 parts of sulphuric acid are required per 85 parts of Chili saltpetre; but if this proportion be maintained in practice the nitric acid will not all be disengaged by the sulphuric acid; an excess of the latter must be taken, and as a rule 80 parts of Chili saltpetre are taken per 98 parts of acid, so that a portion of the latter remains free to the very end of the reaction.

and nitric acid, which is converted into vapour, and may be condensed, because it is a liquid and volatile substance. On a small scale, this reaction may be carried on in a glass retort with a glass condenser. On a large scale, in chemical works, the process is exactly similar, but

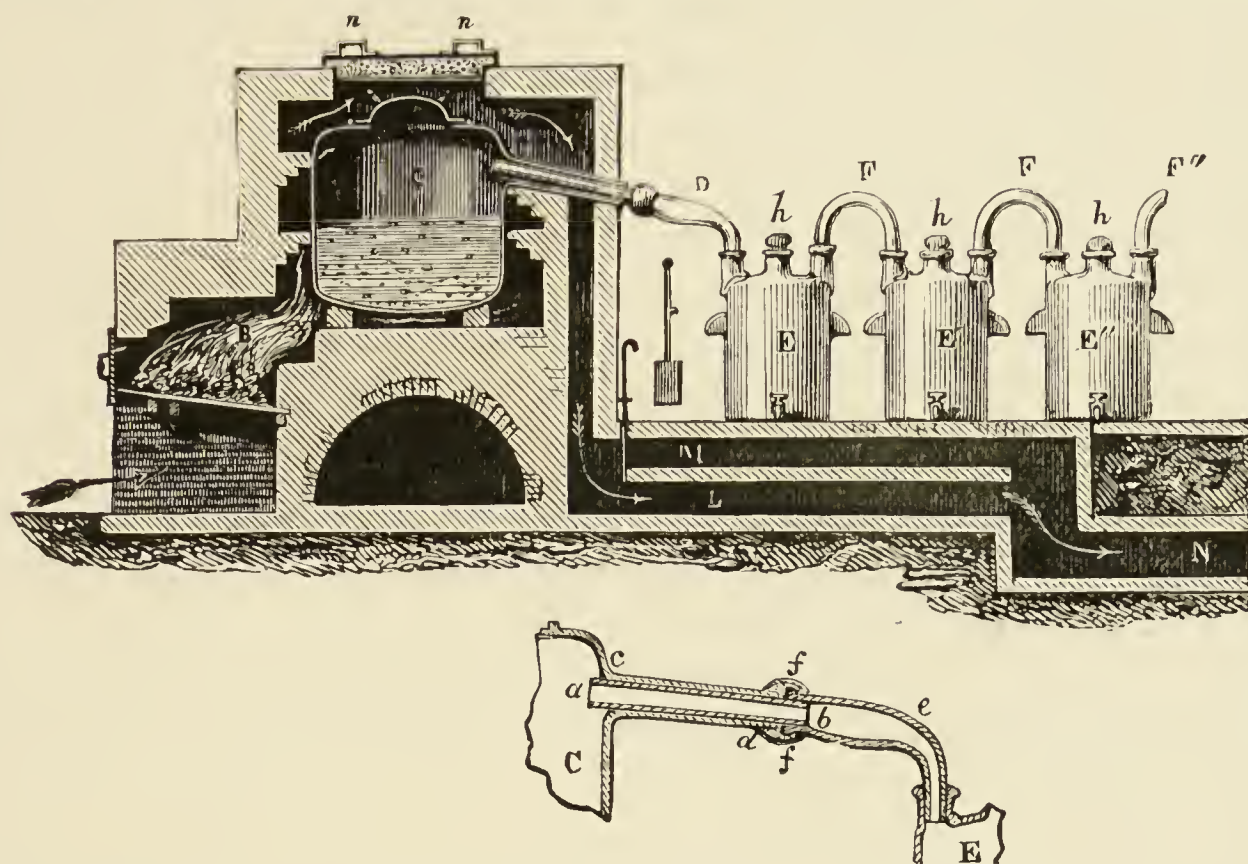


FIG. 55.—Method of preparing nitric acid on a large scale. A cast-iron retort, C, is fixed in the furnace, and heated by the fire, B. The flame and products of combustion are at first led along the flue, M (in order to heat the receivers), and afterwards into L. The retort is charged with Chili saltpetre and sulphuric acid, and the cover luted on with clay and gypsum. A clay tube *a*, is fixed into the neck of the retort (in order to prevent the nitric acid from corroding the cast iron), and a bent glass tube, D, luted on to it. This tube carries the vapours into a series of earthenware receivers, E. Nitric acid mixed with sulphuric acid collects in the first. The purest nitric acid is procured from the second, whilst that which condenses in the third receiver contains hydrochloric acid, and that in the fourth nitrous oxide. Water is poured into the last receiver in order to condense the residual vapours.

iron retorts are employed for holding the mixture of nitre and sulphuric acid, and earthenware three-necked bottles are used instead of a condenser,³⁰ as shown in fig. 55.

³⁰ It must be observed that sulphuric acid, at least when undiluted (60° Baumé), corrodes cast iron with difficulty, so that it may be heated in cast-iron retorts. Nevertheless, both sulphuric and nitric acids have a certain action on cast iron, so that the acid obtained will contain traces of iron. In practice sodium nitrate (Chili saltpetre) is usually employed, as it is cheaper, but in the laboratory it is best to take potassium nitrate, because it is purer and does not froth up so much as sodium nitrate when heated with sulphuric acid. In the action of an excess of sulphuric acid on nitre and nitric acid a portion of the latter is decomposed, forming lower oxides of nitrogen, which are dissolved in the nitric acid. A portion of the sulphuric acid itself is also carried over as spray by the vapours of the nitric acid. Hence sulphuric acid occurs as an impurity in commercial nitric acid. A certain amount of hydrochloric acid will also be found to be present in it, because sodium chloride is generally found as an impurity in nitre, and under the action of sulphuric acid it forms hydrochloric acid. Commercial acid further contains a considerable excess of water above that necessary for the formation of the hydrate, because water is first poured into the earthenware vessels employed for condensing the nitric acid in order to facilitate its cooling and condensation. Further, the

The nitric acid obtained generally contains water. It is extremely difficult to deprive it of all the admixed water without destroying a portion of the acid itself and partially converting it into lower oxides, because in the absence of excess of water it is very unstable. When rapidly distilled a portion is decomposed, giving free oxygen and lower oxides of nitrogen, which, together with the water, remain in solution with the nitric acid. It is therefore necessary to work with great care in order to obtain a pure hydrate of nitric acid, HNO_3 , and to mix the nitric acid obtained from nitre, as above described, with sulphuric acid, which takes up the water, and to distil it at the lowest possible temperature—that is, by lowering the pressure and by placing the retort holding the mixture in a water or oil bath and carefully heating it. The first portion of the nitric acid thus distilled boils at 86° , has a specific gravity at 15° of 1.526, and solidifies at -50° ; it is very unstable at higher temperatures. This is the normal hydrate, HNO_3 , which corresponds with the salts, NMO_3 , of nitric acid. When diluted with water, nitric acid presents a higher boiling-point, not only as compared with that of the nitric acid itself, but also with that of water; so that if very dilute nitric acid be distilled, the first portions passing over will consist of almost pure water, until the boiling-point in the vapours reaches 121° . At this temperature a compound of nitric acid with water, containing about 70 per cent. of nitric acid,³¹ distils over; its specific gravity at 15° is 1.421. If the

acid of composition HNO_3 decomposes with great ease, with the evolution of oxides of nitrogen. Thus the commercial acid contains a large number of impurities, and is frequently purified in the following manner:—Lead nitrate is first added to the acid as it forms non-volatile and almost insoluble (precipitated) substances with the free sulphuric and hydrochloric acids, according to the equations: $\text{Pb}(\text{NO}_3)_2 + 2\text{HCl} = \text{PbCl}_2 + 2\text{HNO}_3$ and $\text{Pb}(\text{NO}_3)_2 + \text{H}_2\text{SO}_4 = \text{PbSO}_4 + 2\text{HNO}_3$. Potassium chromate is then added to the impure nitric acid, by which means oxygen is liberated from the chromic acid, and this oxygen, at the moment of its evolution, oxidises the lower oxides of nitrogen and converts them into nitric acid. A pure nitric acid, containing no impurities other than water, may then be obtained by carefully distilling (under a low pressure) the acid, treated as above described, and particularly if only the middle portions of the distillate are collected. Such acid should give no precipitate, either with a solution of barium chloride (a precipitate shows the presence of sulphuric acid) or with a solution of silver nitrate (a precipitate shows the presence of hydrochloric acid), nor should it, after being diluted with water, give a coloration with starch containing potassium iodide (a coloration shows the admixture of other oxides of nitrogen). The oxides of nitrogen may be most easily removed from impure nitric acid by heating it for some time with a small quantity of pure charcoal. By the action of nitric acid on the charcoal carbonic anhydride is evolved, and this carries off the lower oxides of nitrogen. On re-distilling, pure acid is obtained. The oxides of nitrogen occurring in solution may also be removed by passing air through the nitric acid.

³¹ Dalton, Smith, Bineau, and others considered that the hydrate of nitric acid of constant boiling-point (see Chap. I., note 60) was the compound $2\text{HNO}_3, 3\text{H}_2\text{O}$, but Roscoe showed that its composition changes with a variation of the pressure and temperature under which the distillation proceeds. Thus, at a pressure of 1 atmosphere the solution

solution contain less than 25 per cent. of water, then, the specific gravity of the solution being above 1.44, HNO_3 evaporates off and fumes in the air, forming the above hydrate, whose vapour pressure is less than that of water. Such solutions form *fuming nitric acid*. On distillation this gives monohydrated acid,³² HNO_3 , which is a hydrate boiling at 121° , so that it is obtained from both weak and strong solutions. Fuming nitric acid, under the action not only of organic substances, but even of heat, loses a portion of its oxygen, forming lower oxides of nitrogen, which impart a *reddish-brown colour* to it; ³³ the pure acid is colourless.

of constant boiling-point contains 68.6 per cent., and at one-tenth of an atmosphere 66.8 per cent. of the acid. Judging from what has been said concerning solutions of hydrochloric acid, and from the variation of specific gravity, I think that the comparatively large decrease in the pressure of the vapours depends on the formation of a hydrate, $\text{NHO}_3, 2\text{H}_2\text{O}$ (=53.6 per cent.) Such a hydrate may be expressed by $\text{N}(\text{HO})_5$, that is, as $\text{NH}_4(\text{HO})$, in which all the equivalents of hydrogen are replaced by hydroxyl. The constant boiling-point will then be the temperature of decomposition of this hydrate.

The variation of the specific gravity at 15° from water ($p=0$) to the hydrate $\text{NHO}_3, 5\text{H}_2\text{O}$ (41.2 per cent. HNO_3) is expressed by $s = 9992 + 57.4p + 0.16p^2$, if water = 10,000 at 4° . For example, when $p=30$ per cent., $s=11,860$. For more concentrated solutions, the presence must be assumed of at least the above-mentioned hydrate, $\text{HNO}_3, 2\text{H}_2\text{O}$, of which the specific gravity $s = 9570 + 84.18p - 0.240p^2$; but perhaps (the results of observations of the specific gravity of the solutions not being in sufficient agreement to warrant a conclusion) the hydrate $\text{HNO}_3, 3\text{H}_2\text{O}$ should be recognised, as is indicated by many nitrates (Al, Mg, Co, &c.), which crystallise with this amount of water of crystallisation. From $\text{HNO}_3, 2\text{H}_2\text{O}$ to HNO_3 the specific gravity of the solutions (at 15°) is given by: $s = 10,652 + 62.08p - 0.160p^2$. The hydrate $\text{HNO}_3, 2\text{H}_2\text{O}$ is recognised by Berthelot on the basis of the thermo-chemical data for solutions of nitric acid, because on approaching to this composition there is a rapid change in the amount of heat evolved by mixing nitric acid with water. Pickering (1892) by refrigeration obtained the crystalline hydrates: $\text{HNO}_3, \text{H}_2\text{O}$, melting at -37° and $\text{HNO}_3, 3\text{H}_2\text{O}$, melting at -18° . A more detailed study of the reactions of hydrated nitric acid would no doubt show, on approaching these hydrates, the existence of change in the process and rapidity of reaction.

³² The normal hydrate HNO_3 , corresponding with the ordinary salts, may be termed the monohydrated acid, because the anhydride N_2O_5 forms with water this normal nitric acid. In this sense the hydrate $\text{HNO}_3, 2\text{H}_2\text{O}$ is the pentahydrated acid: $\text{N}_2\text{O}_5 + 5\text{H}_2\text{O}$.

³³ For technical and laboratory purposes recourse is frequently had to *red fuming nitric acid*—that is, the normal nitric acid, HNO_3 , or strong solutions of it (containing less than $1\frac{1}{2}\text{H}_2\text{O}$), containing lower oxides of nitrogen, NO_2 and N_2O_3 , in solution. This acid is prepared by decomposing nitre with half its weight of strong sulphuric acid, or by distilling nitric acid with an excess of sulphuric acid. The normal nitric acid is first obtained, but partially decomposes, and gives the lower oxidation products of nitrogen, which are dissolved by the nitric acid, to which they impart its usual brown or reddish colour. This acid fumes in the air, from which it attracts moisture, forming a less volatile hydrate. If carbonic anhydride be passed through the reddish-brown fuming nitric acid for a long period of time, especially if assisted by a moderate heat, it expels all the lower oxides, and leaves a colourless acid free from these oxides. It is necessary, in the preparation of the red acid, that the receivers should be kept quite cool, because it is only when cold that nitric acid is able to dissolve a large proportion of the oxides of nitrogen. The strong red fuming acid has a specific gravity 1.56 at 20° , and

Nitric acid, as an **acid hydrate**, enters into reactions of double decomposition with bases, basic hydrates (alkalies), and salts. In these cases salts of nitric acid are obtained. An alkali and nitric acid give water and a salt; for instance, with lime, $\text{CaO} + 2\text{HNO}_3 = \text{Ca}(\text{NO}_3)_2 + \text{H}_2\text{O}$.³⁴ The composition of the ordinary salts of nitric acid may be expressed by the general formula $\text{M}(\text{NO}_3)_n$, where M indicates a metal replacing the hydrogen in one or several (n) molecules of nitric acid. We shall find afterwards that the atoms M of metals are equivalent to one (K, Na, Ag) atom of hydrogen, or two (Ca, Mg, Ba), or three (Al, In), or, in general, n atoms of hydrogen. **The salts of nitric acid** are especially characterised by being all **soluble in water**.³⁵ Owing to the property common to all these salts of entering into double decompositions and also to the volatility of nitric acid, they evolve nitric acid when heated with sulphuric acid. They are all, like the acid itself, capable of evolving oxygen when heated, and consequently of acting as oxidising substances; thus, for instance, they deflagrate with ignited carbon, which burns at the expense of the oxygen of the salt, and forms gaseous products of combustion.³⁶

has a suffocating smell of the oxides of nitrogen. When the red acid is mixed with water it turns green, and then bluish, and with an excess of water ultimately becomes colourless. This is owing to the fact that the oxides of nitrogen in the presence of water and nitric acid undergo change, and give coloured solutions.

Marchlewsky (1892) showed that the green solutions contain (besides HNO_3) HNO_2 and N_2O_4 , whilst the blue solutions contain only HNO_2 (see note 48).

The action of red fuming nitric acid (or a mixture of it with sulphuric acid) is in many cases very powerful and rapid, and sometimes quite different from that of pure nitric acid. Thus iron becomes covered with a coating of oxides, and is insoluble in acids; it becomes, as it is said, passive. Also chromic acid (and potassium dichromate) gives oxide of chromium with this red acid, which is thus deoxidised. This is owing to the presence of the lower oxides of nitrogen, which are capable of being oxidised—that is, of passing into nitric acid like the higher oxides. But, generally, the action of fuming nitric acid, both red and colourless, is powerfully oxidising.

³⁴ Hydrogen is not evolved in the action of nitric acid (especially strong) on metals, even with those metals which evolve hydrogen under the action of other acids. This is because at the moment of its separation the hydrogen reduces the nitric acid, with formation of the lower oxides of nitrogen, as we shall see later.

³⁵ Certain basic salts of nitric acid, however (for example, the basic salt of bismuth), are insoluble in water, but, on the other hand, all the normal salts are soluble; this is an exceptional phenomenon among acids, all the ordinary acids forming insoluble salts with one or another base. Thus, of sulphuric acid the salts of barium, lead, &c., of hydrochloric acid the salts of silver, &c., are insoluble in water. However, the normal salts of acetic and certain other acids are all soluble.

³⁶ **Ammonium nitrate**, NH_4NO_3 , is easily obtained by adding a solution of ammonia or of ammonium carbonate to nitric acid until it becomes neutral. On evaporating this solution, crystals of the salt are formed which contain no water of crystallisation. It crystallises in prisms like those formed by common nitre, and has a refreshing taste; 100 parts of water at t° dissolve $54 + 0.61 t$ parts by weight of the salt. It is soluble in alcohol, melts at 160° , and is decomposed at about 180° , forming water and nitrous oxide, $\text{NH}_4\text{NO}_3 = 2\text{H}_2\text{O} + \text{N}_2\text{O}$. If ammonium nitrate is mixed with sulphuric acid, and the

Nitric acid also enters into double decompositions with a number of hydrocarbons, which possess no alkaline characters and do not react with other acids. Under these circumstances the nitric acid gives water and a new substance termed a **nitro-compound**. The chemical character of the nitro-compound is the same as that of the original substance; for example, if an indifferent substance be taken, the nitro-compound obtained from it will also be indifferent; whilst if an acid be taken, an acid will be obtained.^{36a} Benzene, C_6H_6 , for instance, acts according to the equation: $C_6H_6 + HNO_3 = H_2O + C_6H_5NO_2$, nitrobenzene being produced. The substance taken, C_6H_6 , is a liquid hydrocarbon which has a faint tarry smell, boils at 80° , and is lighter than water; the action of nitric acid yields nitrobenzene, which is a substance boiling at about 210° , heavier than water, and having an almond-like odour: it is employed in large quantities for the preparation of aniline and aniline dyes.³⁷ As the

mixture heated to about the boiling-point of water, nitric acid is evolved, and ammonium hydrogen sulphate remains in solution; but if the mixture be heated rapidly to 160° , nitrous oxide will be evolved. In the first case the sulphuric acid takes up ammonia, and in the second place water. Ammonium nitrate is employed in practice for the artificial production of cold, because in dissolving in water it lowers the temperature very considerably. For this purpose it is best to take equal parts by weight of the salt and water. The salt must first be reduced to a powder and then rapidly stirred up in the water, when the temperature will fall from $+15^\circ$ to -10° , so that the water freezes.

Ammonium nitrate absorbs ammonia, with which it forms unstable compounds resembling compounds containing water of crystallisation [Divers (1872), Raoult (1873)]. At -10° , $NH_4NO_3 \cdot 2NH_3$ is formed; it is a liquid of sp. gr. 1.15, which loses all its ammonia under the influence of heat. At $+28^\circ$, $NH_4NO_3 \cdot NH_3$ is formed as a solid which easily parts with its ammonia when heated, especially in solution.

Troost (1882) investigated the dissociation pressures of the compounds formed, and came to the conclusion that a definite compound corresponding to the formula $2NH_4NO_3 \cdot 3NH_3$ is formed, because the pressure of dissociation remains constant in the decomposition of such a compound at 0° . V. Kouriloff (1893), however, considers that the constancy of the pressure of the ammonia evolved is due to the decomposition of a saturated solution, and not of a definite compound. During decomposition the system is composed of a liquid and a solid, and the pressure only becomes constant from the moment the solid begins to precipitate. The composition $2NH_4NO_3 \cdot 3NH_3$ corresponds with a saturated solution at 0° , and the solubility of NH_4NO_3 in NH_3 increases with a rise of temperature.

^{36a} This is explained by saying that in true nitro-compounds the residue of nitric acid NO_2 takes the place of the hydrogen in the hydrocarbon group. For example, if C_6H_5OH be given, then $C_6H_4(NO_2)OH$ will be a true nitro-compound having the radical properties of C_6H_5OH . If, on the other hand, the NO_2 replace the hydrogen of the aqueous radicle ($C_6H_5ONO_2$), the chemical character is changed, as in the passage of KOH into $KONO_2$ (nitre) (see note 37 and Organic Chemistry).

³⁷ The compound ethers of nitric acid in which the hydrogen of the aqueous radicle (OH) is replaced by the residue of nitric acid (NO_2) are frequently called nitro-compounds. But in their chemical character they differ from true nitro-compounds (for details see Organic Chemistry) and do not burn like them. The action of nitric acid on cellulose, $C_6H_{10}O_5$, is an example. This substance, which forms the outer coating of all plant cells, occurs in an almost pure state in cotton, in common writing

nitro-compounds contain both combustible elements (hydrogen and carbon), as well as oxygen in unstable combination with nitrogen, in the form of the radicle NO_2 of nitric acid, they decompose, when ignited or even when struck, with an explosion, owing to the pressure of the vapours and gases formed—free nitrogen, carbonic anhydride, CO_2 , carbonic oxide CO , and aqueous vapour. In the explosion of nitro-compounds ^{37a}

paper, and in flax, &c.; under the action of nitric acid it yields water and nitrocellulose (like water and KNO_3 from KHO), which, although it has the same appearance as the cotton originally taken, differs from it entirely in properties. It explodes when struck, bursts into flame very easily under the action of sparks, and acts like gunpowder, whence its name of pyroxylin, or gun-cotton. The composition of gun-cotton is $\text{C}_6\text{H}_7\text{N}_3\text{O}_{11} = \text{C}_6\text{H}_{10}\text{O}_5 + 3\text{NHO}_3 - 3\text{H}_2\text{O}$. The proportion of the group NO_2 in nitrocellulose may be decreased by limiting the action of the nitric acid, compounds being then obtained with different properties; for instance the (impure) well-known *collodion cotton*, containing from 11 to 12 per cent. of nitrogen, and *pyro-collodion* (Mendeléeff, 1890), containing from 12.5 to 12.4 per cent. of nitrogen. Both these products are soluble in a mixture of alcohol and ether (in collodion a portion of the substance is soluble in alcohol), and the solution when evaporated gives a transparent film, which is insoluble in water. A solution of collodion is employed in medicine for covering wounds, and in wet-plate photography for giving on glass an even coating of a substance into which the various reagents employed in the process are introduced. The composition of pyro-collodion, $\text{C}_{30}\text{H}_{38}(\text{NO}_2)_{12}\text{O}_{25}$ (i.e. a product of the substitution of 12 atoms of hydrogen by the residue of nitric acid NO_2 in $5\text{C}_6\text{H}_{10}\text{O}_5$), is such that when exploded the whole of its hydrogen is capable of forming water and all its carbon, carbon monoxide, CO , occupying a larger volume than would be occupied by the CO_2 formed from the same amount of oxygen (because $\text{CO}_2 = 2$ vols. and $\text{CO} = 2$ vols., and consequently $2\text{CO} = 4$ vols.). Therefore the normal (in the absence of subsidiary reactions) decomposition of pyro-collodion is expressed by the equation: $\text{C}_{30}\text{H}_{38}(\text{NO}_2)_{12}\text{O}_{25} = 30\text{CO} + 19\text{H}_2\text{O} + 6\text{N}_2$. As the form of nitrocellulose which evolves the greatest quantity (by volume) of vapours and gases (from a given weight of nitrocellulose), pyro-collodion presents one of the most convenient smokeless powders for artillery, all the more so because experiments made at the Russian Admiralty Research Laboratory (see the Admiralty Magazine for 1895) show that properly prepared ribbons of this powder burn when exploded in successive layers (which is required in firing guns to prevent them from bursting), and that it may be kept for an indefinite period if well washed in water, notwithstanding that it contains 58 per cent. of oxygen.

^{37a} The property possessed by nitroglycerin (occurring in dynamite), nitrocellulose, and the other nitro-compounds, of burning with an explosion, and their employment for smokeless powder and as explosives in general, is explained in the same way as the deflagration and explosion of a mixture of nitre and charcoal; in both cases the elements of the nitric acid occurring in the compound are decomposed, the oxygen in burning uniting with the carbon, and the nitrogen being set free; thus a very large volume of gaseous substances (nitrogen and oxides of carbon) is rapidly formed from the solid substances originally taken. These gases occupy an incomparably larger volume than the original substance, and therefore produce a powerful pressure and explosion. It is evident from their power of exploding with the development of heat (that is, in decomposing, not with the absorption of energy, as is generally the case, but with the evolution of energy), that the nitro-compounds form stores of energy which are readily set free, and that consequently their elements occur in a state of particularly energetic motion, which is especially strong in the group NO_2 ; this group is common to all nitro-compounds, and all the oxygen compounds of nitrogen are unstable, easily decomposable, and (note 28) absorb heat in their formation. On the other hand, the nitro-compounds are instructive as an example and proof of the fact that the elements and groups forming compounds are united in definite order in the molecules of a compound. A blow, con-

much heat is evolved, as in the combustion of gunpowder or detonating gas, and the force of explosion in a closed space is great, because from a solid or liquid nitro-compound occupying a small space there are

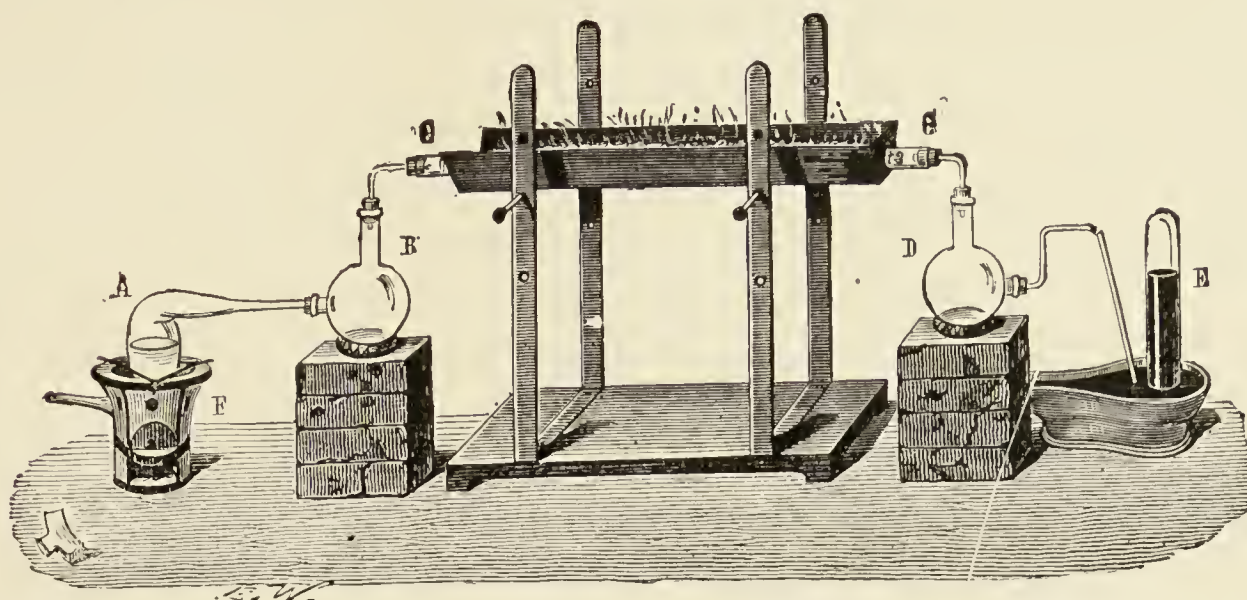


FIG. 56.—The method of decomposition of nitrous anhydride, also applicable to the other oxides of nitrogen, and to their analysis. NO_2 is generated from nitrate of lead in the retort A. Nitric acid and other less volatile products are condensed in B. The tube CC contains copper, and is heated from below. Undecomposed volatile products (if any are formed) are condensed in D, which is cooled. If the decomposition is incomplete, brown fumes make their appearance in this receiver. The gaseous nitrogen is collected in the cylinder E.

formed only vapours and gases, the pressure of which is great, not merely on account of the small space in which they are formed, but

cussion, or rise of temperature is necessary to bring the combustible elements C and H into the most intimate contact with NO_2 , and to distribute the elements in a new order in new compounds.

As regards the composition of the nitro-compounds, it will be seen that the hydrogen of a given substance is replaced by the complex group NO_2 of the nitric acid. The same is observed in the passage of alkalis into nitrates, so that the reactions of substitution of nitric acid—that is, the formation of salts and nitro-compounds—may be expressed in the following manner. In these cases the hydrogen is replaced by the so-called **radicle of nitric acid** NO_2 , as is evident from the following table:—

{ Caustic potash	KHO .	{ Glycerin	$\text{C}_3\text{H}_5\text{H}_3\text{O}_3$.
{ Nitre	$\text{K}(\text{NO}_2)\text{O}$.	{ Nitroglycerin	$\text{C}_3\text{H}_5(\text{NO}_2)_3\text{O}_3$.
{ Hydrate of lime	CaH_2O_2 .	{ Phenol	$\text{C}_6\text{H}_5\text{OH}$.
{ Calcium nitrate	$\text{Ca}(\text{NO}_2)_2\text{O}_2$.	{ Picric acid	$\text{C}_6\text{H}_2(\text{NO}_2)_3\text{OH}$, &c.

The difference between the salts formed by nitric acid and the nitro-compounds consists in the fact that nitric acid is very easily separated from the salts of nitric acid by means of sulphuric acid (that is, by a method of double saline decomposition), whilst nitric acid is not displaced by sulphuric acid from true nitro-compounds; for instance, nitrobenzene, $\text{C}_6\text{H}_5\text{NO}_2$. As nitro-compounds are formed exclusively from hydrocarbons, they are described with them in organic chemistry.

The group NO_2 of nitro-compounds in many cases (like all the oxidised compounds of nitrogen) passes into the ammonia group or the ammonia radicle NH_2 . This requires the action of reducing substances evolving hydrogen: $\text{RNO}_2 + 6\text{H} = \text{RNH}_2 + 2\text{H}_2\text{O}$. Thus Zinin converted nitrobenzene, $\text{C}_6\text{H}_5\text{NO}_2$, into aniline, $\text{C}_6\text{H}_5\text{NH}_2$, by the action of hydrogen sulphide.

Admitting the existence of the group NO_2 , as replacing hydrogen in various compounds, nitric acid may be considered as water in which half the hydrogen is replaced by the radicle of nitric acid. In this sense nitric acid is nitro-water, $(\text{NO}_2)\text{OH}$, and its anhydride dinitro-water, $(\text{NO}_2)_2\text{O}$. In nitric acid the radicle of nitric acid is

owing also to the high temperature corresponding to the decomposition (explosive combustion) of the nitro-compound.³⁸

If the vapour of nitric acid is passed through an even moderately heated glass tube, the formation of dark-brown fumes of the lower oxides of nitrogen and the separation of free oxygen may be observed, $2\text{NHO}_3 = \text{H}_2\text{O} + 2\text{NO}_2 + \text{O}$. Even light produces a similar decomposition, but not a complete one. The decomposition is complete at a white heat, when nitrogen is formed: $2\text{NHO}_3 = \text{H}_2\text{O} + \text{N}_2 + \text{O}_5$. Hence it is easily understood that nitric acid may part with its oxygen to a number of substances capable of being oxidised.³⁹ It is consequently

combined with hydroxyl, just as in nitrobenzene it is combined with the radicle of benzene.

It should here be remarked that the group NO_3 may be recognised in the salts of nitric acid, because the salts have the composition $\text{M}(\text{NO}_3)_n$, just as the metallic chlorides have the composition MCl_n . But the group NO_3 does not form any other compounds beyond the salts, and therefore it should be considered as hydroxyl, HO , in which H is replaced by NO_2 .

³⁸ The nitro-compounds play a very important part in mining and artillery. Detailed accounts of them must be looked for in special works, among which the works of A. R. Shuliachenko and T. M. Chelltsoff occupy an important place in the Russian literature on this subject, although historically the scientific works of Abel in England and Berthelot in France stand pre-eminent. The latter elucidated much in connection with explosive compounds by a series of both experimental and theoretical researches. Among explosives particularly important places from a practical point of view are occupied by ordinary or black gunpowder (Chap. XIII., note 16), fulminating mercury (Chap. XVI., note 26), the different forms of gun-cotton (Chap. VI., note 37), and nitro-glycerin (Chap. VIII., note 45, and Chap. XII., note 33). The latter when mixed with solid pulverulent substances, like magnesia, tripoli, &c., forms dynamite, which is so largely used in quarries and mines, in driving tunnels, &c. We may add that the simplest true nitro-compound, that is, marsh gas, CH_4 , in which all the hydrogens are replaced by NO_2 groups, $\text{C}(\text{NO}_2)_4$ has been obtained by L. N. Shishkoff, as well as nitroform, $\text{CH}(\text{NO}_2)_3$.

³⁹ Nitric acid may be completely decomposed by passing its vapour over highly incandescent copper, because the oxides of nitrogen first formed give up their oxygen to the

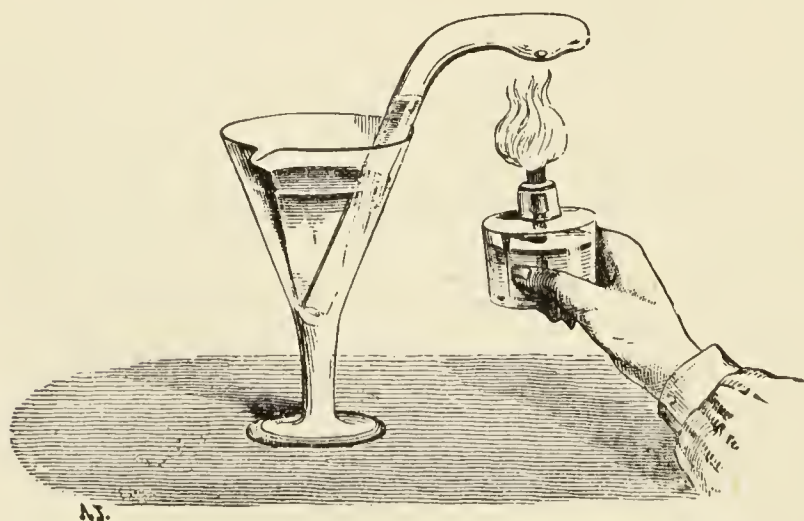


FIG. 57.—Decomposition of nitrous oxide by sodium.

red-hot metallic copper, so that water and nitrogen gas alone are obtained. This forms a means for determining the composition both of nitric acid and of all the other compounds of nitrogen with oxygen, because by collecting the gaseous nitrogen formed it is possible from its volume to calculate its weight, and consequently its amount in a given quantity of a nitrogenous substance; and by weighing the copper before and after the decomposition it is possible to determine the amount of oxygen by the in-

crease in weight. The complete decomposition of nitric acid is also accomplished by passing a mixture of hydrogen and nitric acid vapours through a red-hot tube. Sodium

an **oxidising agent**. Charcoal, as we have already seen, burns in nitric acid; phosphorus, sulphur, iodine, and the majority of metals also decompose nitric acid, some on heating and others even at the ordinary temperature: the substances taken are oxidised and the nitric acid is deoxidised, yielding compounds containing less oxygen.

A few metals, such as gold and platinum, do not act on nitric acid, but the majority decompose it; in so doing, an oxide of the metal is formed, which, if it has the character of a base, acts on the remaining nitric acid; hence, with the majority of metals, the result of the reaction is usually not an oxide of the metal, but the corresponding salt of nitric acid, and, at the same time, one of the lower oxides of nitrogen. The resulting salts of the metals are soluble, and hence it is said that nitric acid *dissolves* nearly all metals.⁴⁰ This is termed the *solution* of metals by acids, although it is not a case of simple solution, but a complex chemical change of the substances taken. When treated with this acid, those metals whose oxides do not combine with nitric acid yield the oxide itself, and not a salt; for example, tin acts in this manner on nitric acid, forming a hydrated oxide, SnH_2O_3 , which is obtained in the form of a white powder: $\text{Sn} + 4\text{HNO}_3 = \text{H}_2\text{SnO}_3 + 4\text{NO}_2 + \text{H}_2\text{O}$. Silver is able to take up still more oxygen, and to convert a large proportion of nitric acid into nitrous anhydride: $4\text{Ag} + 6\text{HNO}_3 = 4\text{AgNO}_3 + \text{N}_2\text{O}_3 + 3\text{H}_2\text{O}$. Copper takes up still more oxygen from nitric acid, converting it into nitric oxide, and, by the action of zinc, nitric acid is able to give up a still further quantity of oxygen, forming nitrous oxide: $4\text{Zn} + 10\text{HNO}_3 = 4\text{Zn}(\text{NO}_3)_2 + \text{N}_2\text{O} + 5\text{H}_2\text{O}$.⁴¹ Sometimes, and especially

also decomposes the oxides of nitrogen at a red heat, taking up all the oxygen. This method is sometimes used for determining the composition of the oxides of nitrogen.

⁴⁰ The application of this acid for etching copper or steel in engraving is based on this fact. The copper is covered with a coating of wax, resin, &c. (etching ground), on which nitric acid does not act, and which is afterwards removed in certain parts with a needle, and the whole then washed in nitric acid. The parts coated remain untouched whilst the uncovered portions are eaten into by the acid. Copper plates for etchings, aquatints, &c., are prepared in this manner.

⁴¹ The formation of such complex equations as the above often presents some difficulty to the beginner. It should be observed that if the reacting and resultant substances be known, it is easy to form an equation for the reaction. Thus, if we wish to form an equation expressing the fact that nitric acid acting on zinc gives nitrous oxide, N_2O , and zinc nitrate, $\text{Zn}(\text{NO}_3)_2$, we must reason as follows:—Nitric acid contains hydrogen, whilst the salt and nitrous oxide do not; hence water is formed, and therefore it is as though anhydrous nitric acid, N_2O_5 , were acting. For its conversion into nitrous oxide it parts with four equivalents of oxygen, and hence it is able to oxidise four equivalents of zinc and thus convert them into zinc oxide, ZnO . These four equivalents of zinc oxide require for their conversion into the salt four more equivalents of nitric anhydride; consequently five equivalents in all of the latter are required, or ten equivalents of nitric acid. Thus in order to express the reaction in whole numbers of equivalents ten equivalents of nitric acid are necessary and four equivalents of zinc. It must not be forgotten, however, that there are very few such reactions which can be entirely expressed

with dilute solutions of nitric acid, the deoxidation proceeds as far as the formation of hydroxylamine and ammonia, and in some cases it leads to the formation of nitrogen itself. The formation of one or other nitrogenous substance from nitric acid is determined not only by the nature of the reacting substances, but also by the relative masses of water and nitric acid, and also by the temperature and pressure, that is, by the sum total of the conditions of reaction; and as in a given mixture even these conditions vary (the temperature and the relative masses vary), it not unfrequently happens that a mixture of different deoxidation products of nitric acid is formed.

Thus the action of nitric acid on metals consists in their being oxidised, whilst the acid itself is converted, according to the temperature, the concentration in which it is taken, the nature of the metal, &c., into lower oxides, ammonia, or even into nitrogen.⁴² Many compounds are oxidised by nitric acid like metals and other elements; for instance, lower oxides are converted into higher oxides. Thus, arsenious acid is converted into arsenic acid, suboxide of iron into oxide, sulphurous acid

by simple equations. The majority of equations of reactions only express the chief and ultimate products of reaction, and thus none of the three preceding equations express all that actually occurs in the action of metals on nitric acid. In no one of them is one oxide of nitrogen alone formed, but always several, either together or consecutively—according to the temperature and strength of the acid. And this is easily intelligible. The resulting oxide is itself capable of acting on metals and of being deoxidised, and in the presence of the nitric acid it may change the acid and be itself changed. The equations given must be looked on as a systematic expression of the main features of the reactions, or as a limit towards which they tend, but to which they only attain in the absence of disturbing influences.

⁴² Montemartini endeavours to show that the products evolved in the action of nitric acid upon metals (and their amount) are in direct connection with both the concentration of the acid and the capacity of the metals to decompose water. Those metals which only decompose water at a high temperature give, under the action of nitric acid, NO_2 , N_2O_4 , and NO ; whilst those metals which decompose water at a lower temperature give, besides the above products, N_2O , N , and NH_3 ; and, lastly, the metals which decompose water at the ordinary temperature also evolve hydrogen. Nitric acid diluted with a large quantity of water does not oxidise copper, but it oxidises tin; dilute nitric acid also does not oxidise either silver or mercury; but, on the addition of nitrous acid, even dilute acid acts on the above metals. This naturally depends on the less stability of nitrous acid, and on the fact that after the commencement of the action the nitric acid is itself converted into nitrous acid, which continues to act on the silver and mercury. Veley (Oxford, 1891) made detailed researches on the action of nitric acid upon Cu , Hg , and Bi , and showed that nitric acid of 30 per cent. strength does not act upon these metals at the ordinary temperature if nitrous acid (traces of which are destroyed by urea) and oxidising agents such as H_2O_2 , KClO_3 , &c. are entirely absent; but in the presence of even a small amount of nitrous acid the metals form nitrites, which, with HNO_3 , form nitrates and the oxides of nitrogen, which re-form the nitrous acid necessary for starting the reaction, because the reaction, $2\text{NO} + \text{HNO}_3 + \text{H}_2\text{O} = 3\text{HNO}_2$, is reversible. The above metals are quickly dissolved in a 1 per cent. solution of nitrous acid. Moreover, Veley observed that nitric acid is partially converted into nitrous acid by gaseous hydrogen in the presence of the nitrates of Cu and Pb .

into sulphuric acid, the sulphides of the metals, M_2S , into sulphates, M_2SO_4 , &c.; in a word, nitric acid brings about oxidation, its oxygen being taken up and transferred to many other substances. Certain substances are oxidised by strong nitric acid so rapidly and with so great an evolution of heat that they deflagrate and burst into flame. Thus turpentine, $C_{10}H_{16}$, bursts into flame when poured into fuming nitric acid. In virtue of its oxidising property, nitric acid *removes the hydrogen* from many substances. Thus it decomposes hydriodic acid, separating the iodine and forming water; and if fuming nitric acid be poured into a flask containing gaseous hydriodic acid, a rapid reaction takes place, accompanied by flame and the separation of violet vapours of iodine and brown fumes of oxides of nitrogen.⁴³

As nitric acid is very easily decomposed with the separation of oxygen, it was for a long time supposed that it was not capable of forming the corresponding **nitric anhydride**, N_2O_5 ; but first of all, Deville, and subsequently Weber and others, discovered the methods of its formation. Deville obtained nitric anhydride by decomposing silver nitrate by chlorine at a moderate heat. Chlorine acts on the above salt at a temperature of 95° ($2AgNO_3 + Cl_2 = 2AgCl + N_2O_5 + O$), and when once the reaction is started, it continues by itself without further heating. Brown fumes are given off, which are condensed in a tube surrounded by a freezing-mixture. A portion condenses in this tube and a portion remains in the gaseous state; the latter contains free oxygen. A crystalline mass and a liquid substance are obtained in the tube; the liquid is poured off, and a current of dry carbonic acid gas passed through the apparatus in order to remove all traces of volatile substances (liquid oxides of nitrogen) adhering to the crystals of nitric anhydride. These form a voluminous mass of rhombic crystals (density 1.64), which are sometimes of rather large size; they melt at about 30° and distil at about 47° . In distilling, a portion of the substance is

⁴³ When nitric acid acts on many organic substances it often happens that not only is hydrogen removed from them, but also oxygen introduced; thus, for example, nitric acid converts toluene, C_7H_8 , into benzoic acid, $C_7H_6O_2$. In certain cases, also, a portion of the carbon contained in an organic substance burns at the expense of the oxygen of the nitric acid. So, for instance, phthalic acid, $C_8H_6O_4$, is obtained from naphthalene, $C_{10}H_8$. Thus the action of nitric acid on the hydrocarbons is often most complex; not only does nitration take place, but also separation of carbon, displacement of hydrogen, and combination of oxygen. There are few organic substances which can withstand the action of nitric acid, and it causes fundamental changes in a number of them. It leaves a yellow stain on the skin, and in large quantity causes a wound and entirely eats away the membranes of the body. The tissues of plants are eaten into with the greatest ease by strong nitric acid in just the same manner. One of the most durable blue vegetable dyes employed in dyeing tissues is *indigo*; yet it is readily *converted into a yellow substance* by the action of nitric acid, and small traces of free nitric acid may be recognised by this means.

decomposed. With water these crystals give nitric acid. Nitric anhydride is also obtained by the action of phosphoric anhydride, P_2O_5 , on cold pure nitric acid (below 0°). During the very careful distillation of equal parts by weight of these two substances a portion of the acid decomposes, giving a liquid compound, $H_2O, 2N_2O_5 = N_2O_5, 2HNO_3$, whilst the greater part of the nitric acid gives the anhydride according to the equation: $2HNO_3 + P_2O_5 = 2PHO_3 + N_2O_5$. On heating, nitric anhydride decomposes either with an explosion, or gradually, into nitric peroxide and oxygen: $N_2O_5 = N_2O_4 + O$.

Nitrogen peroxide, N_2O_4 , and **nitrogen dioxide**, NO_2 , express one and the same composition, but they should be distinguished like ordinary oxygen and ozone, although in this case their mutual conversion is more easily effected and takes place on vaporisation; also, O_3 loses heat on passing into O_2 , whilst N_2O_4 absorbs heat in forming NO_2 .

Nitric acid in acting on tin and on many organic substances (for example starch) yields brown vapours, consisting of a mixture of N_2O_3 and NO_2 . A purer product is obtained by the decomposition of lead nitrate by heat, $Pb(NO_3)_2 = 2NO_2 + O + PbO$, when non-volatile lead oxide, oxygen gas, and nitrogen dioxide are formed. The latter condenses, in a well-cooled vessel, to a brown liquid, which boils at about 22° . The purest peroxide of nitrogen, solidifying at -9° , is obtained by mixing dry oxygen in a freezing-mixture with twice its volume of dry nitric oxide, NO , when transparent prisms of nitrogen peroxide are formed in the receiver: they melt into a colourless liquid at about -10° . When the temperature of the receiver is above -9° , the crystals melt,⁴⁴ and at 0° give a reddish-yellow liquid, like that obtained in the decomposition of lead nitrate. The vapours of nitrogen peroxide have a characteristic odour, and at the ordinary temperature are of a dark-brown colour, but at lower temperatures the colour of the vapour is much fainter. When heated, especially above 50° , the colour becomes a very dark brown, so that the vapours almost lose their transparency.

The causes of these peculiarities of nitrogen peroxide were not clearly understood until Deville and Troost determined the density and dissociation of the vapour of this substance at different temperatures, and showed that the density varies. If the density is referred to that

⁴⁴ According to certain investigations, if a brown liquid is formed from the melted crystals by heating above -9° , then they no longer solidify at -10° , probably because a certain amount of N_2O_3 (and oxygen) is formed, and the liquid does not solidify, even at -30° , or it may be that the passage from $2NO_2$ into N_2O_4 is not so easily accomplished as the passage from N_2O_4 into $2NO_2$.

Liquid nitrogen peroxide (that is, a mixture of NO_2 and N_2O_4) is employed in admixture with hydrocarbons as an explosive.

of hydrogen at the same temperature and pressure, it is found to vary from 38 at the boiling-point, or about 27° , to 23 at 135° , after which the density remains constant up to those high temperatures at which the oxides of nitrogen are decomposed. As on the basis of the laws enunciated in the following chapter, the density 23 corresponds with the compound NO_2 (because the weight corresponding with this molecular formula is 46, and the density referred to hydrogen as unity is equal, as we shall presently see, to half the molecular weight); at temperatures above 135° the existence of nitrogen dioxide only must be recognised. It is this gas which is of a brown colour. At a lower temperature it forms nitrogen peroxide, N_2O_4 , whose molecular weight, and therefore density, is twice that of the dioxide. This substance, which is polymeric with nitrogen dioxide, as ozone is polymeric with oxygen, and has twice as great a vapour density (46 referred to hydrogen), is formed in greater quantity the lower the temperature, and crystallises at -10° . The reasons both of the variation of the colour of the gas (N_2O_4 gives colourless and transparent vapours, whilst those of NO_2 are brown and opaque) and the variation of the vapour density with the variation of temperature are thus made quite clear; and as at the boiling-point a density 38 was obtained, at that temperature the vapours consist of a mixture of 79 parts by weight of N_2O_4 with 21 parts by weight of NO_2 .⁴⁵ It is evident that a decomposition here takes place, the peculiarity of which consists in the fact that the product of decomposition, NO_2 , is polymerised (i.e. becomes denser, combines with itself) at a lower temperature; that is, the reaction



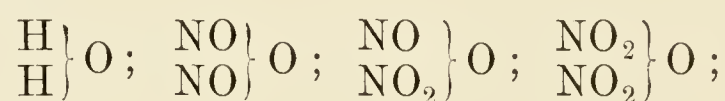
is a reversible reaction, and consequently the whole phenomenon represents a **dissociation** in a homogeneous gaseous medium, where the original substance, N_2O_4 , and the resultant, NO_2 , are both gases. The *measure of dissociation* will be expressed if we find the proportion of the quantity of the substance decomposed to the whole amount of the substance. At the boiling-point, therefore, the measure of the decomposition of nitrogen peroxide will be 21 per cent.; at 135° it = 1, and at 10° it = 0, the N_2O_4 then being not decomposable. Consequently the limits of dissociation at the atmospheric pressure are -10° and 135° .⁴⁶ Within the limits of these temperatures the

⁴⁵ Because if x equal the amount by weight of N_2O_4 , its volume will = $x/46$, and the amount of NO_2 will = $100 - x$, and consequently its volume will = $(100 - x)/23$. But the mixture, having a density 38, will weigh 100; consequently its volume will = $100/38$. Hence $x/46 + (100 - x)/23 = 100/38$, or $x = 79.0$.

⁴⁶ The phenomena and laws of dissociation, which we shall consider only in particular instances, are discussed in detail in works on theoretical chemistry. Nevertheless, in

vapours of nitrogen peroxide have not a constant density; but, on the other hand, above and below these limits, definite substances exist. Thus, above 135° , N_2O_4 has ceased to exist and NO_2 alone remains. It is evident that at the ordinary temperature there is a partially dissociated system or a mixture of nitrogen peroxide, N_2O_4 , and nitrogen dioxide, NO_2 . In the brown liquid boiling at 22° probably a portion of the N_2O_4 has already passed into NO_2 , and it is only the colourless liquid and crystalline substance at -10° that can be considered as pure nitrogen peroxide.⁴⁷

The above explains the action of nitrogen peroxide on water at low temperatures. N_2O_4 then acts on water like a mixture of the anhydrides of nitrous and nitric acids. The first, N_2O_3 , may be looked upon as water in which each of the two atoms of hydrogen is replaced by the radicle NO , while in the second each hydrogen is replaced by the radicle NO_2 , belonging to nitric acid; and in nitrogen peroxide one atom of the hydrogen of water is replaced by NO and the other by NO_2 , as is seen from the formulæ—



or $\text{H}_2\text{O} ; \text{N}_2\text{O}_3 ; \text{N}_2\text{O}_4 ; \text{N}_2\text{O}_5.$

In fact, nitrogen peroxide at low temperatures gives with water (ice) both nitric, HNO_3 , and nitrous, HNO_2 , acids. The latter, as we shall

respect to nitrogen peroxide, as an historically important example of dissociation in a homogeneous gaseous medium, we will cite the results of the careful investigations (1885–1886) of E. and L. Natanson, who determined the densities under various conditions of temperature and pressure. The degree of dissociation, expressed as above (it may also be expressed otherwise—for example, by the ratio of the quantity of substance decomposed to that unaltered), proves to increase at all temperatures as the pressure diminishes, which would be expected for a homogeneous gaseous medium, as a decreasing pressure aids the formation of the lightest product of dissociation (that having the least density or largest volume). Thus in the Natansons' experiments the degree of dissociation at 0° increases from 10 per cent. to 30 per cent., with a decrease of pressure of from 251 to 38 mm.; at 49.7° it increases from 49 per cent. to 93 per cent. with a fall of pressure of from 498 to 27 mm., and at 100° it increases from 89.2 per cent. to 99.7 per cent. with a fall of pressure from 732.5 to 11.7 mm. At 130° and 150° the decomposition is complete—that is, only NO_2 remains at the low pressures (less than the atmospheric) at which the Natansons made their determinations; but it is probable that at higher pressures (of several atmospheres) molecules of N_2O_4 would still be formed, and it would be exceedingly interesting to trace the phenomena under the conditions both of very considerable pressures and of relatively large volumes.

⁴⁷ Liquid nitrogen peroxide is said by Geuther to boil at 22° – 26° , and to have a sp. gr. = 1.494 at 0° and 1.474 at 15° . It is evident that, in the liquid as in the gaseous state, the variation of density with the temperature depends not only on physical, but also on chemical changes, as the amount of N_2O_4 decreases and the amount of NO_2 increases as the temperature rises, and they (as polymeric substances) should have different densities, just as is the case, for instance, with the hydrocarbons C_5H_{10} and $\text{C}_{10}\text{H}_{20}$.

It may not be superfluous to mention here that the measurement of the specific heat

afterwards see, splits up into water and the anhydride, N_2O_3 . If, however, warm water acts on nitrogen peroxide, only nitric acid and monoxide of nitrogen are formed: $3\text{NO}_2 + \text{H}_2\text{O} = \text{NO} + 2\text{HNO}_3$.

Although NO_2 is not decomposed into N and O even at 500° , still in many cases it acts as an oxidising agent. Thus, for instance, it oxidises mercury, converting it into mercurous nitrate, $2\text{NO}_2 + \text{Hg} = \text{HgNO}_3 + \text{NO}$, being itself deoxidised into nitric oxide, into which the dioxide passes in many other instances, and from which it is easily formed.⁴⁸

Nitrous anhydride, N_2O_3 , corresponds⁴⁹ with nitrous acid, NHO_2 , which forms a series of salts, the nitrites—for example, the sodium salt NaNO_2 ,^{49a} the ammonium salt $(\text{NH}_4)\text{NO}_2$,⁵⁰ the silver salt AgNO_2 ,⁵¹ &c. Neither the anhydride nor the hydrate of the acid is

of a mixture of the vapours of N_2O_4 and NO_2 enabled Berthelot to determine that the transformation of 2NO_2 into N_2O_4 is accompanied by the evolution of about 13,000 units of heat, and as the reaction proceeds with equal facility in either direction, it will be exothermal in the one direction and endothermal in the other; and this clearly demonstrates the possibility of reactions taking place in either direction, although, as a rule, reactions evolving heat proceed with the greater ease.

⁴⁸ Nitric acid of sp. gr. 1.51 in dissolving nitrogen peroxide becomes brown, whilst nitric acid of sp. gr. 1.32 is coloured greenish blue, and acid of sp. gr. less than 1.15 remains colourless after absorbing nitrogen peroxide (note 33).

⁴⁹ Nitrogen peroxide as a mixed substance has no corresponding independent salts, but Sabatier and Senderens (1892) showed that, under certain conditions, NO_2 combines directly with some metals—for instance, copper and cobalt—forming Cu_2NO_2 and CoNO_2 as dark brown powders, which do not, however, exhibit the reactions of salts. Thus by passing gaseous nitrogen dioxide over freshly reduced (from the oxidised compounds by heating with hydrogen) copper at 25° – 30° , Cu_2NO_2 is directly formed. With water it partly gives off NO_2 and partly forms nitrite of copper, leaving metallic copper and its suboxide. The nature of these compounds has not yet been sufficiently investigated.

^{49a} This sodium salt, NaNO_2 , is the most largely used in the arts, as it reacts with the amides of certain colouring matters forming dyes for tissues. It is called ‘nitrite,’ and is prepared in the same way as KNO_2 (see further on).

⁵⁰ Ammonium nitrite may be easily obtained in solution by a method of double decomposition (for instance, of the barium salt with ammonium sulphate) similar to that employed for the other salts of nitrous acid, but it decomposes with great ease when evaporated, with evolution of gaseous nitrogen, as already mentioned (Chap. V.). If the solution, however, is evaporated at the ordinary temperature under the receiver of an air-pump, a solid saline mass is obtained, which is easily decomposed when heated. The dry salt even decomposes with an explosion when struck, or when heated to about 70° : $\text{NH}_4\text{NO}_2 = 2\text{H}_2\text{O} + \text{N}_2$. It is also formed by the action of aqueous ammonia on a mixture of nitric oxide and oxygen, or by the action of ozone on ammonia, and in many other instances. Sørensen (1894) prepared NH_4NO_2 by the action of a mixture of N_2O_3 and other oxides of nitrogen on lumps of ammonium carbonate, extracting the nitrite of ammonium formed with absolute alcohol, and precipitating it from this solution by ether. This salt is crystalline, dissolves in water with absorption of heat, and attracts moisture from the air. In order to preserve the salt it should be covered with a layer of pure dry ether.

⁵¹ Silver nitrite, AgNO_2 , is obtained as a very slightly soluble substance, which is precipitated, on mixing solutions of silver nitrate, AgNO_3 , and potassium nitrite, KNO_2 . It

known in a perfectly pure state. The anhydride has only been obtained as a very unstable substance, and has not yet been fully investigated; and on attempting to obtain the acid NHO_2 from its salts, it always gives water and the anhydride, whilst the latter, as an intermediate oxide, partially or wholly splits up into $\text{NO} + \text{NO}_2$. But the salts of nitrous acid are distinguished for their great stability. Potassium nitrate, KNO_3 , may be converted into potassium nitrite by depriving it of a portion of its oxygen; for instance, by fusing it (at not too high a temperature) with metals such as lead, $\text{KNO}_3 + \text{Pb} = \text{KNO}_2 + \text{PbO}$.^{51a} The resultant salt is soluble in water, whilst the oxide of lead is insoluble. With sulphuric and other acids the solution of potassium nitrite⁵² immediately evolves a brown gas, nitrous anhydride: $2\text{KNO}_2 + \text{H}_2\text{SO}_4 = \text{K}_2\text{SO}_4 + \text{N}_2\text{O}_3 + \text{H}_2\text{O}$. The same gas (N_2O_3) is obtained by passing nitric oxide at 0° through liquid nitrogen tetroxide,⁵³ or by heating starch with nitric acid of sp. gr. 1.3. At a very low temperature it condenses into a blue liquid boiling at about 0° ,⁵⁴ but then partially decomposing into $\text{NO} + \text{NO}_2$. Nitrous anhydride possesses a remarkable capacity for oxidising. Ignited bodies burn in it; nitric acid absorbs it, and then acquires the property of acting on silver and other metals, even when diluted (see note 42). **Potassium iodide** is oxidised by this gas just as it is by ozone (and by peroxide of hydrogen, chromic and other acids, but not by dilute nitric acid or sulphuric acid), with the **separation of iodine**. This iodine may be

is soluble in a large volume of water, and this is taken advantage of to free it from silver oxide, which is also present in the precipitate, owing to the fact that potassium nitrite always contains a certain amount of oxide, which with water gives the hydroxide, forming oxide of silver with silver nitrate. The solution of silver nitrite gives, by double decomposition with metallic chlorides (for instance, barium chloride), insoluble silver chloride and the nitrite of the metal taken (in this case, barium nitrite, $\text{Ba}(\text{NO}_2)_2$).

^{51a} Leroy (1889) obtained KNO_2 by mixing powdered KNO_3 with BaS , igniting the mixture in a crucible and washing the fused salts; BaSO_4 is then left as an insoluble residue, and KNO_2 passes into solution: $4\text{KNO}_3 + \text{BaS} = 4\text{KNO}_2 + \text{BaSO}_4$.

⁵² Probably potassium nitrite, KNO_2 , when strongly heated, especially with metallic oxides, evolves N and O , and yields potassium oxide, K_2O , because nitre is liable to such a decomposition; but it has, as yet, been but little investigated.

⁵³ The reaction $\text{N}_2\text{O}_3 = \text{NO}_2 + \text{NO}$ is probably reversible, i.e. resembles the conversion of N_2O_4 into NO_2 . The brown colour of the fumes of N_2O_3 is due to the formation of NO_2 .

If nitrogen peroxide is cooled to -20° , and half its weight of water added to it drop by drop, the tetroxide is decomposed, as we have already stated, into nitrous and nitric acids; the former does not then remain as a hydrate, but straightway passes into the anhydride, and hence if the resultant liquid be slightly warmed vapours of nitrous anhydride, N_2O_3 , are evolved, and condense into a blue liquid, as was shown by Fritzsche. This method of preparing nitrous anhydride apparently gives the purest product, but it easily dissociates, forming NO and NO_2 (and therefore also nitric acid, if water is present).

⁵⁴ According to Thorpe, N_2O_3 boils at $+18^\circ$. Geuther gives the boiling-point as $+3.5^\circ$, and the sp. gr. at 0° as 1.449.

recognised (Chapter IV.) by its turning starch blue. Very small traces of nitrites may be easily detected by this method. If, for example, starch and potassium iodide are added to a solution of potassium nitrite (at first there will be no change, there being no free nitrous acid), and then sulphuric acid, the nitrous acid (or its anhydride) set free liberates iodine, which produces a blue colour with the starch. Nitric acid does not act in this manner, but in the presence of zinc the coloration takes place, which proves the formation of nitrous acid in the deoxidation of nitric acid.⁵⁵ Nitrous acid acts directly on ammonia, forming nitrogen and water, $\text{HNO}_2 + \text{NH}_3 = \text{N}_2 + 2\text{H}_2\text{O}$.⁵⁶

As nitrous anhydride easily splits up into $\text{NO}_2 + \text{NO}$, so, like NO_2 , with warm water it gives nitric acid and nitric oxide, according to the equation: $3\text{N}_2\text{O}_3 + \text{H}_2\text{O} = 4\text{NO} + 2\text{HNO}_3$.

Being in a lower degree of oxidation than nitric acid, nitrous acid and its anhydride are oxidised in solution by many oxidising substances—for example, by potassium permanganate—into nitric acid.⁵⁷

Nitric oxide, NO.—This permanent gas⁵⁸ (that is unliquefiable by pressure without the aid of cold) may be obtained by the deoxidation of any of the above-described compounds of nitrogen with oxygen. The deoxidation of nitric acid by metals is the usual method employed for its preparation. Dilute nitric acid (sp. gr. 1.18 but not stronger, as then N_2O_3 and NO_2 are produced) is poured into a flask containing

⁵⁵ In its oxidising action nitrous anhydride gives nitric oxide, $\text{N}_2\text{O}_3 = 2\text{NO} + \text{O}$. Thus its analogy to ozone becomes still more marked, because in ozone it is only one-third of the oxygen that acts in oxidising; from O_3 there is obtained O , which acts as an oxidiser, and common oxygen O_2 . In a physical aspect the relation between N_2O_3 and O_3 is revealed in the fact that both substances are of a blue colour when in the liquid state.

⁵⁶ This reaction is taken advantage of for converting the amides, NH_2R (where R is an element or a complex group), into hydroxides, RHO . In this case $\text{NH}_2\text{R} + \text{HNO}_2$ forms $2\text{N} + \text{H}_2\text{O} + \text{RHO}$; H_2N is replaced by HO , the radicle of ammonia by the radicle of water. This reaction is employed for transforming many nitrogenous organic substances having the properties of amides into their corresponding hydroxides. Thus aniline, $\text{C}_6\text{H}_5\text{NH}_2$, which is obtained from nitrobenzene, $\text{C}_6\text{H}_5\text{NO}_2$ (note 37), is converted by nitrous anhydride into phenol, $\text{C}_6\text{H}_5\text{OH}$, which occurs in the creosote extracted from coal tar. Thus the H of the benzene is successively replaced by NO_2 , NH_2 , and HO ; this method is suitable for other cases also. With the acid amides of the aromatic series of hydrocarbons, nitrous acid gives highly coloured diazo-compounds.

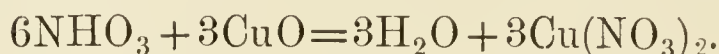
⁵⁷ The action of a solution of potassium permanganate, KMnO_4 , on nitrous acid in the presence of sulphuric acid is determined by the fact that the higher oxide of manganese, Mn_2O_7 , contained in the permanganate is converted into the lower oxide, MnO , which as a base forms manganese sulphate, MnSO_4 , while the oxygen serves for the oxidation of HNO_2 into HNO_3 . As the solution of the permanganate is of a red colour, whilst that of manganese sulphate is almost colourless, this reaction is clearly seen, and may be employed for the detection and determination of nitrous acid and its salts.

⁵⁸ The absolute boiling-point = -93° (see Chap. II., note 29). The liquefied gas boils at -142° , and the melting-point is -152° .

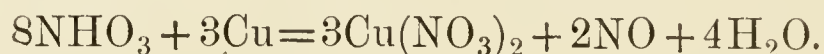
metallic copper.⁵⁹ The reaction commences at the ordinary temperature. Mercury and silver also give nitric oxide with nitric acid. In these reactions with metals one portion of the nitric acid is employed in the oxidation of the metal, whilst the other, and by far the greater, portion combines with the metallic oxide so obtained, with formation of the nitrate corresponding with the metal taken. The first action of the copper on the nitric acid is thus expressed by the equation :



The second reaction consists in the formation of copper nitrate—



Adding these two equations together we obtain :



Nitric oxide is a colourless gas which is only slightly soluble in water ($\frac{1}{20}$ of a volume at the ordinary temperature). Reactions of double decomposition in which nitric oxide readily takes part are not known—that is to say, it is an indifferent, not a saline, oxide. Like the other oxides of nitrogen, it is decomposed into its elements at a red heat (starting from 900° , 60 per cent. of it forms N_2 and $2\text{N}_2\text{O}_3$ at 1200° , but complete decomposition into N_2 and O_2 only takes place at the melting-point of platinum; Emich, 1892). The most characteristic property of nitric oxide is its capacity for directly and easily combining with oxygen (with evolution of heat). With **oxygen** it forms **nitrous anhydride** and **nitrogen peroxide** : $2\text{NO} + \text{O} = \text{N}_2\text{O}_3$; $2\text{NO} + \text{O}_2 = 2\text{NO}_2$.

⁵⁹ Kammerer proposed preparing nitric oxide, NO, by pouring a solution of sodium nitrate over copper shavings and adding sulphuric acid drop by drop. The oxidation of ferrous salts by nitric acid also gives NO. One part of strong hydrochloric acid is taken and iron is dissolved in it (FeCl_2), and then an equal quantity of hydrochloric acid and also nitre are added to the solution. On heating, nitric oxide is evolved. In the presence of an excess of sulphuric acid and mercury the conversion of nitric acid into nitric oxide is complete (that is, the reaction proceeds to the end, and the nitric oxide is obtained without other products), and upon this is founded one of the methods for determining nitric acid (in nitrometers of various kinds, described in text-books of analytical chemistry), as the amount of NO can be easily and accurately measured volumetrically. The amount of nitrogen in gun-cotton, for instance, is determined by dissolving it in sulphuric acid. Nitrous acid acts in the same manner. Upon this property Emich (1892) founds his method for preparing pure NO. He pours mercury into a flask, and then covers it with sulphuric acid, in which a certain amount of NaNO_2 or other substance corresponding to HNO_2 or HNO_3 has been dissolved. The evolution of NO proceeds at the ordinary temperature, becoming more rapid as the surface of the mercury is increased (if the flask is shaken, the reaction proceeds very rapidly). If the gas is passed over KHO, it is obtained quite pure, because KHO does not act upon NO at the ordinary temperature (if heated, KNO_2 and N_2O or N_2 are formed).

If nitric oxide is mixed with oxygen and immediately shaken up with caustic potash, it is almost entirely converted into potassium nitrite; whilst after a certain time, when the formation of N_2O_4 has already commenced, a mixture of potassium nitrite and nitrate is obtained. If oxygen is passed into a bell-jar filled with nitric oxide, brown fumes of N_2O_3 and N_2O_2 are formed, even in the absence of moisture; in presence of water these give, as we already know, nitric acid and nitric oxide, so that with excess of water and oxygen the whole of the nitric oxide is easily and directly converted into nitric acid. This reaction of the re-formation of nitric acid from nitric oxide, air, and water, $2\text{NO} + \text{H}_2\text{O} + \text{O}_3 = 2\text{HNO}_3$, is frequently made use of in practice. The experiment showing the conversion of nitric oxide into nitric acid is very striking and instructive. As the intermixture of the oxygen with the oxide of nitrogen proceeds, the nitric acid formed dissolves in water, and if an excess of oxygen has not been added, the whole of the gas (nitric oxide), being converted into HNO_3 , is absorbed, and the water entirely fills the bell-jar previously containing the gas.⁶⁰ It is evident that nitric oxide⁶¹ in combining with oxygen has a strong tendency to give the higher types of nitrogen compounds, which we see in nitric acid, HNO_3 or $\text{NO}_2(\text{OH})$, in nitric anhydride, N_2O_5 or $(\text{NO}_2)_2\text{O}$, and in ammonium chloride, NH_4Cl . If X stand for an atom of hydrogen, or its equivalents, chlorine, hydroxyl, &c., and if O, which is, according to the law of substitution, equivalent to H_2 , be indicated by X_2 , then the three compounds of nitrogen above named should be considered as compounds of the type or form NX_5 . For example, in nitric acid

⁶⁰ This transformation of the permanent gases, nitric oxide and oxygen, into liquid nitric acid in the presence of water, and with the evolution of heat, presents a most striking instance of liquefaction produced by the action of chemical forces. The latter perform with ease the work which physical (cooling) and mechanical (pressure) forces effect only with difficulty. In this the motion, which is so distinctively the property of the gaseous molecules, is apparently destroyed.

⁶¹ Nitric oxide is capable of entering into many characteristic combinations; it is absorbed by the solutions of many acids—for instance, tartaric, acetic, phosphoric, sulphuric—and metallic chlorides (for example, SbCl_5 , BiCl_3 , &c., with which it forms definite compounds; Besson 1889), and also by the solutions of many salts, especially those formed by suboxide of iron (for instance, ferrous sulphate). In this case a brown compound is formed which is exceedingly unstable, like all the analogous compounds of nitric oxide. Ammonia is obtained by the action of a caustic alkali on the resultant compound, because the oxygen of the nitric oxide and water are transferred to the ferrous oxide, forming ferric oxide, whilst the nitrogen combines with the hydrogen of the water. According to the investigations of Gay (1885), the compound is formed with the evolution of a large quantity of heat, and is easily dissociated, like a solution of ammonia in water. If the presence of a radicle NO_2 , of the composition of nitrogen peroxide, must be recognised in the compounds of nitric acid, then a radicle NO , having the composition of nitric oxide, may be admitted in compounds of nitrous acid. The compounds in which the radicle NO is recognised are called *nitroso-compounds*. These substances are described in Prof. Bunge's work (Kief, 1868).

$X_5 = O_2 + (OH)$, where $O_2 = X_4$, and $OH = X$; whilst nitric oxide is a compound of the form NX_2 . Hence this lower form, like lower forms in general, strives by combination to attain to the higher forms proper to the compounds of a given element. NX_2 passes consecutively into NX_3 —namely, into N_2O_3 and NHO_2 — NX_4 (for instance, NO_2) and NX_5 .^{61a}

As the decomposition of nitric oxide begins at temperatures above 900° , **many substances burn in it**; thus, ignited phosphorus continues to burn in nitric oxide, but sulphur and charcoal are extinguished in it. This is due to the fact that the heat evolved in the combustion of these two substances is insufficient for the decomposition of the nitric oxide, whilst the heat developed by burning phosphorus suffices to produce this decomposition. That nitric oxide really supports combustion, owing to its being decomposed by the action of heat, is proved by the fact that strongly ignited charcoal continues to burn in the same nitric oxide⁶² in which a feebly incandescent piece of charcoal is extinguished.

The compounds of nitrogen with oxygen, which we have so far considered, may all be prepared from nitric oxide, and may themselves be converted into it. Thus nitric oxide stands in intimate connection with them.⁶³ The passage of nitric oxide into the higher degrees of

^{61a} In this example we see an instance of variable atomicity, of which we shall have further occasion to speak, especially in Chap. X., note 1.

⁶² A mixture of nitric oxide and hydrogen is inflammable. If a mixture of the two gases be passed over spongy platinum the nitrogen and hydrogen even combine, forming ammonia. A mixture of nitric oxide with many combustible vapours and gases is very inflammable. A very characteristic flame is obtained on burning a mixture of nitric oxide and the vapour of the combustible carbon bisulphide, CS_2 . The latter substance is very volatile, so that it is sufficient to pass the nitric oxide through a layer of the carbon bisulphide (for instance, in a Woulfe's bottle) in order that the gas escaping should contain a considerable amount of the vapours of this substance. This mixture continues to burn when ignited, and the flame emits a large quantity of the so-called ultra-violet rays, which are capable of inducing chemical combinations and decompositions, and therefore the flame may be employed in photography in the absence of sufficient daylight (magnesium light and electric light have the same property). There are many gases (for instance, ammonia) which when mixed with nitric oxide explode in a eudiometer.

⁶³ The oxides of nitrogen naturally do not proceed directly from oxygen and nitrogen by contact alone, because their formation is accompanied by the absorption of a large quantity of heat, for (see note 29) about 21,500 heat units are absorbed when 16 parts of oxygen and 14 parts of nitrogen combine; consequently the decomposition of nitric oxide into oxygen and nitrogen is accompanied by the evolution of this amount of heat; and therefore with nitric oxide, as with all explosive substances and mixtures, the reaction once started is able to proceed by itself. In fact, Berthelot remarked the decomposition of nitric oxide in the explosion of fulminate of mercury. This decomposition does not take place spontaneously; substances even burn with difficulty in nitric oxide, probably because a certain portion of the nitric oxide in decomposing gives oxygen, which combines with another portion of nitric oxide, and forms nitric peroxide, a somewhat more stable compound of nitrogen and oxygen. The further combinations of nitric oxide with

oxidation and the converse reaction is employed in practice as a means for **transferring the oxygen of the air** to substances capable of being oxidised. Starting with nitric oxide, it may easily be converted, with the aid of the oxygen of the atmosphere and water, into nitric acid, N_2O_3 , and NO_2 , and by their means employed to oxidise other substances. In this oxidising action nitric oxide is again formed, and it may again be converted into nitric acid, and so on continuously, if only oxygen and water be present. Hence the fact, which at first appears to be a paradox, that by means of a small quantity of nitric oxide in the presence of oxygen and water it is possible to oxidise an indefinitely large quantity of substances which cannot be directly oxidised, either by the action of the atmospheric oxygen or by the action of nitric oxide itself. The sulphurous anhydride, SO_2 , which is obtained in the combustion of sulphur and in roasting many metallic sulphides in the air, is an example of this kind. In practice this gas is obtained by burning sulphur or iron pyrites, FeS_2 , the latter being thereby converted into oxide of iron and sulphurous anhydride, SO_2 . In contact with the oxygen of the atmosphere this gas does not pass into the higher degree of oxidation, sulphuric anhydride, SO_3 ,^{63a} and if it does form sulphuric acid with water and the oxygen of the atmosphere, $\text{SO}_2 + \text{H}_2\text{O} + \text{O} = \text{H}_2\text{SO}_4$, it does so very slowly. With nitric acid (and especially with nitrous acid, but not with nitrogen tetroxide) and water, sulphurous anhydride, on the contrary, very easily forms sulphuric acid, and especially so when slightly heated (about 40°), the nitric acid (or, better still, nitrous acid) being converted into nitric oxide—

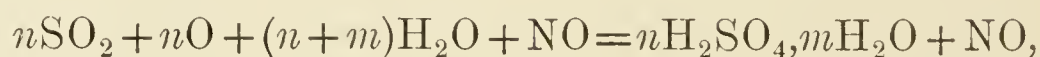


The presence of water is absolutely indispensable here, otherwise sulphuric anhydride is formed, which combines with the oxides of nitrogen (nitrous anhydride), forming a crystalline substance containing oxides of nitrogen (*chamber crystals*, which will be described in Chapter XX). Water destroys this compound, forming sulphuric acid and separating the oxides of nitrogen. The water must be taken in a greater quantity than that required for the formation of the hydrate H_2SO_4 , because the latter absorbs oxides of nitrogen. With an excess of water, however, solution does not take place. If, in the above reaction, only water, sulphurous anhydride, and nitric or nitrous

oxygen all proceed with the evolution of heat, and take place spontaneously by contact with air alone. It is evident from these examples that the application of thermochemical data is limited.

^{63a} But in the presence of spongy platinum (and other contact agents), and when heated, SO_2 does form SO_3 with the oxygen of air. This is now taken advantage of for the manufacture of sulphuric acid. See Chap. XX. (the contact process).

acid be taken in a definite quantity, then a definite quantity of sulphuric acid and nitric oxide will be formed, according to the preceding equation; but there the reaction ends, and the excess of sulphurous anhydride, if there be any, will remain unchanged. But if we add air and water, then the nitric oxide will unite with the oxygen to form nitrogen peroxide, and the latter with water to form nitric and nitrous acids, which again give sulphuric acid from a fresh quantity of sulphurous anhydride. Nitric oxide is again formed, which is able to start the oxidation afresh if there be sufficient air. Thus it is possible with a definite quantity of nitric oxide to convert an indefinitely large quantity of sulphurous anhydride into sulphuric acid, water and oxygen only being required.⁶⁴ This may be easily demonstrated by an experiment on a smaller scale, if a certain quantity of nitric oxide be first introduced into a flask, and sulphurous anhydride, steam, and oxygen be then continually passed in. Thus the above-described reaction may be expressed in the following manner:



if we consider only the original substances and those finally formed. In this way a definite quantity of nitric oxide may serve for the conversion of an indefinite quantity of sulphurous anhydride, oxygen, and water into sulphuric acid. In reality, however, there is a limit to this, because air, and not pure oxygen, is employed for the oxidation, so that it is necessary to remove the nitrogen of the air and to introduce a fresh quantity of air. A certain quantity of nitric oxide will pass away with this nitrogen, and will in this way be lost.⁶⁵

⁶⁴ The instance of the action of a small quantity of NO in inducing a definite chemical reaction between large masses ($\text{SO}_2 + \text{O} + \text{H}_2\text{O} = \text{H}_2\text{SO}_4$) is very instructive, because the details relating to it have been studied, and show that intermediate forms of reaction may be discovered in the so-called contact or catalytic phenomena. The essence of the matter here is that A ($=\text{SO}_2$) reacts upon B ($=\text{O}$ and H_2O) in the presence of C, because it gives BC, a substance which forms AB with A, and again liberates C. Consequently C is a medium, a transferring substance, without which the reaction does not proceed. Many similar phenomena may be found in other departments of life. Thus the merchant is an indispensable medium between the producer and the consumer; experiment is a medium between the phenomena of nature and the cognisant faculties, and language, customs, and laws are media which are as necessary for the exchanges of social intercourse as nitric oxide for those between sulphurous anhydride and oxygen and water.

⁶⁵ If the sulphurous anhydride be prepared by roasting iron pyrites, FeS_2 , then each equivalent of pyrites (equivalent of iron, 56, of sulphur 32, of pyrites 120) requires six equivalents of oxygen (that is, 96 parts) for the conversion of its sulphur into sulphuric acid (for forming $2\text{H}_2\text{SO}_4$ with water), besides $1\frac{1}{2}$ equivalent (24 parts) for converting the iron into oxide, Fe_2O_3 ; hence the combustion of the pyrites for the formation of sulphuric acid and ferric oxide requires the introduction of an equal weight of oxygen (120 parts of oxygen to 120 parts of pyrites), or five times its weight of air, of which four

The preceding series of changes serves as the basis of the **manufacture of sulphuric acid** or so-called **chamber acid**. This acid is prepared on a very large scale in chemical works, because it is the cheapest

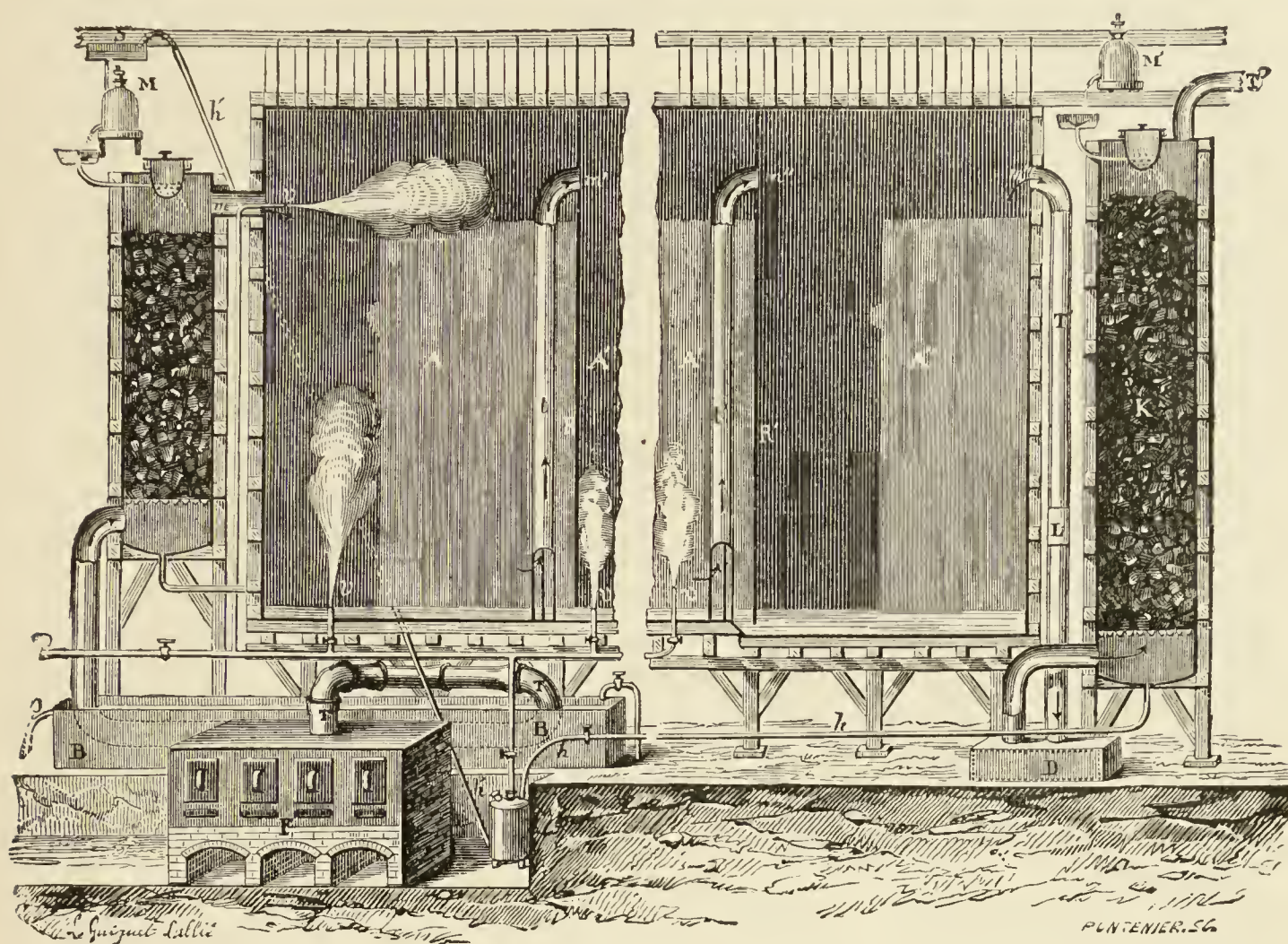


FIG. 58.—Section of sulphuric acid chambers, the first and last chambers only being represented. The tower to the left is called the Glover's tower, and that on the right the Gay-Lussac's tower. Less than $\frac{1}{100}$ th of the natural size.

acid whose action can be applied in a great number of cases. It is therefore used in immense quantities.

The process is carried on in a series of chambers (or in one divided by partitions as in fig. 58, which shows the beginning and end of a

(the four-fifths of nitrogen) will remain inactive, and in the removal of the exhausted air will carry off the remaining nitric oxide. If not all, at least a large portion of the nitric oxide may be collected by passing the escaping air, still containing some oxygen, through substances which absorb oxides of nitrogen. Sulphuric acid itself may be employed for this purpose if it be used in the form of the hydrate H_2SO_4 , or containing only a small amount of water, because such sulphuric acid dissolves the oxides of nitrogen. They may be easily expelled from this solution by heating or by dilution with water, as they are only slightly soluble in aqueous sulphuric acid. Besides which, sulphurous anhydride acts on such sulphuric acid, being oxidised at the expense of the nitrous anhydride, and forming nitric oxide from it, which again enters into the cycle of action. For this reason, the sulphuric acid which has absorbed the oxides of nitrogen escaping from the chambers in the tower κ (see fig. 58) is led back into the first chamber, where it comes into contact with sulphurous anhydride, by which means the oxides of nitrogen are re-introduced into the reaction which proceeds in the chambers. This is the use of the towers (Gay-Lussac's and Glover's) which are erected at either end of the chambers.

chamber) constructed of sheet lead. These chambers are placed one against the other, and communicate by tubes or special orifices so placed that the inlet tubes are in the upper portion of the chamber, and the outlet in the lower and opposite end. The current of steam and gases necessary for the preparation of the sulphuric acid passes through these chambers and tubes. The acid as it is formed falls to the bottom of the chambers or runs down their walls, and flows from chamber to chamber (from the last towards the first), to permit of which the partitions do not reach to the bottom. The floor and walls of the chambers should therefore be made of a material on which the sulphuric acid will not act. Among the ordinary metals lead is the only one suitable.^{65a}

For the formation of the sulphuric acid it is necessary to introduce sulphurous anhydride, steam, air, and nitric acid, or some oxide of nitrogen, into the chambers. The sulphurous anhydride is produced by burning sulphur or iron pyrites. This is carried on in the furnace with four hearths to the left of the drawing. Air is led into the chambers and furnace through orifices in the furnace doors. The current of air and oxygen is regulated by opening or closing these orifices to a greater or less extent. The ingoing draught in the chambers is brought about owing to heated gases and vapours passing into the chambers, whose temperature is further raised by the reaction itself, and also by the remaining nitrogen being continually withdrawn from the outlet (above the tower κ) by a tall chimney situated near the chambers. Nitric acid is prepared from a mixture of sulphuric acid and Chili saltpetre, in the furnaces in which the sulphurous anhydride is evolved (or in special furnaces). Not more than eight parts of nitre are taken to every 100 parts of sulphur burnt. On leaving the furnace the vapours of nitric acid and oxides of nitrogen mixed with air and sulphurous anhydride first pass along the horizontal tubes τ into the receiver $B B$, which is partially cooled by water flowing in on the right-hand side and running out on the left by o , in order to reduce the temperature of the gases entering the chamber. The gases then pass up a tower filled with coke, shown to the left of the drawing. In this tower are placed lumps of coke (the residue from the dry distillation of coal), over which sulphuric acid trickles from the reservoir m . This acid has absorbed in the end tower κ the oxides of nitrogen escaping from the chamber. This end tower is also filled with coke, over which a stream of strong sulphuric acid trickles from

^{65a} Other metals, such as iron, copper, zinc, are corroded by it; glass and china are not acted upon, but they crack from the variations of temperature taking place in the chambers, besides which they are more difficult to join properly than lead; wood, &c., becomes charred.

the reservoir M' . The acid spreads over the coke, and, owing to the large surface offered by the latter, absorbs the greater part of the oxides of nitrogen escaping from the chambers. The sulphuric acid in passing down the tower becomes saturated with the oxides of nitrogen, and flows out at h into a special receiver (in the drawing situated by the side of the furnaces), from which it is forced by steam pressure up the tubes $h' h'$ into the reservoir M , situated above the first tower. The gases passing through this tower (hot) from the furnace, on coming into contact with the sulphuric acid, take up the oxides of nitrogen contained in it, and these are thus returned to the chamber and again participate in the reaction. The sulphuric acid left after the extraction of these oxides flows into the chambers. Thus, on leaving the first coke tower the sulphurous anhydride, air, and vapours of nitric acid and of the oxides of nitrogen pass through the upper tube m into the chamber. Here they come into contact with steam introduced by lead tubes into various parts of the chamber. The reaction takes place in the presence of water, the sulphuric acid falls to the bottom of the chamber, and the same process takes place in the following chambers until the whole of the sulphurous anhydride is consumed. A somewhat greater proportion of air than is strictly necessary is passed in, in order that no sulphurous anhydride should be left unaltered for want of sufficient oxygen. The presence of an excess of oxygen is shown by the colour of the gases escaping from the last chamber. If they be of a pale colour it indicates an insufficiency of air (and the presence of sulphurous anhydride), as otherwise peroxide of nitrogen would be formed. A very dark colour shows a large excess of air, which is also disadvantageous, because it increases the inevitable loss of nitric oxide by increasing the mass of the escaping gases.⁶⁶

⁶⁶ By this means as much as 2,500,000 kilograms of chamber acid, containing about 60 per cent. of the hydrate H_2SO_4 and about 40 per cent. of water, may be manufactured per year in one plant of 5,000 cubic metres capacity (without stoppages). This process has been brought to such a degree of perfection that as much as 300 parts of the hydrate H_2SO_4 are obtained from 100 parts of sulphur, the theoretical amount being not greater than 306 parts. The acid parts with its excess of water on heating. For this purpose it is heated in lead vessels. However, the acid containing about 75 per cent. of the hydrate (60° Baumé) already begins to act on the lead when heated, and therefore the further removal of water is conducted by evaporating in glass or platinum vessels, as will be described in Chap. XX. The aqueous acid (50° Baumé) obtained in the chambers is termed chamber acid. The acid concentrated to 60° Baumé is more generally employed, and sometimes the hydrate (66° Baumé) termed vitriol acid is also used. In England alone more than 1,000 million kilograms of chamber acid are produced by this method. The formation of sulphuric acid by the action of nitric acid was discovered by Drebbel, and the first lead chamber was erected by Roebuck, in Scotland, in the middle of the eighteenth century. The essence of the process was only brought to light at the beginning of the last century, when many improvements were introduced into practice.

Nitrous oxide, N_2O ,⁶⁷ is similar to water in its volumetric composition. Two volumes of nitrous oxide are formed from two volumes of nitrogen and one volume of oxygen, as may be shown by the ordinary method for the analysis of the oxides of nitrogen (by passing them over red-hot copper or sodium). In contradistinction to the other oxides of nitrogen, it is not directly oxidised by oxygen, but it may be obtained from the higher oxides of nitrogen by the action of certain deoxidising substances; thus, for example, a mixture of two volumes of nitric oxide and one volume of sulphurous anhydride, if left in contact with water and spongy platinum, is converted into sulphuric acid and nitrous oxide, $2\text{NO} + \text{SO}_2 + \text{H}_2\text{O} = \text{H}_2\text{SO}_4 + \text{N}_2\text{O}$. Nitric acid, also, under the action

⁶⁷ If the hydrate HNO_3 corresponds to N_2O_5 , the hydrate HNO , **hyponitrous acid**, corresponds to N_2O , and in this sense N_2O is **hyponitrous anhydride**. Hyponitrous acid, NHO , was obtained in the form of its corresponding salts RNO , or $\text{R}_2\text{N}_2\text{O}_2$, by Divers. They are prepared by the reduction of nitrous (and consequently of nitric) salts by sodium amalgam. If this amalgam be added to a cold solution of an alkaline nitrite until the evolution of gas ceases, and the excess of alkali be saturated with acetic acid, an insoluble yellow precipitate of silver hyponitrite, NAgO , will be obtained on adding a solution of silver nitrate. This hyponitrite is insoluble in cold acetic acid, and decomposes when heated, with evolution of nitrous oxide. If rapidly heated it decomposes with an explosion. It is dissolved unchanged by weak mineral acids, whilst the stronger acids (for example, sulphuric and hydrochloric acids) decompose it with the evolution of nitrogen, nitric and nitrous acids remaining in solution. Among the other salts of hyponitrous acid, HNO , those of lead, copper, and mercury are insoluble in water. Judging by the bond existing between hyponitrous acid and the other compounds of nitrogen, there is reason for thinking that its formula should be doubled, $\text{N}_2\text{H}_2\text{O}_2$. For instance, Thum (1893) on gradually oxidising hydroxylamine, $\text{NH}_2(\text{OH})$, into nitrous acid, $\text{NO}(\text{OH})$ (note 25), by means of an alkaline solution of KMnO_4 , first obtained hyponitrous acid, $\text{N}_2\text{H}_2\text{O}_2$, and then a peculiar intermediate acid, $\text{N}_2\text{H}_2\text{O}_3$, which, by further oxidation, gave nitrous acid. On the other hand, Wislicenus (1893) showed that in the action of the sulphuric acid salt of hydroxylamine upon nitrite of sodium, there is formed, besides nitrous oxide (according to V. Meyer, NH_3O , $\text{H}_2\text{SO}_4 + \text{NaNO}_2 = \text{NaHSO}_4 + 2\text{H}_2\text{O} + \text{N}_2\text{O}$), a small amount of hyponitrous acid which may be precipitated in the form of the silver salt; and this reaction is most simply expressed by taking the doubled formula of hyponitrous acid, $\text{NH}_2(\text{OH}) + \text{NO}(\text{OH}) = \text{H}_2\text{O} + \text{N}_2\text{H}_2\text{O}_2$. The best argument in favour of the doubled formula is the property possessed by hyponitrous acid of forming acid salts, HNaN_2O_2 (Zorn), and also the determination of its molecular weight in solution by the method described in the following chapter.

According to Thum, the following are the properties of hyponitrous acid. When liberated from the dry silver salt by the action of dry sulphuretted hydrogen, hyponitrous acid is unstable, and easily explodes even at low temperatures. But when dissolved in water (having been formed by the action of hydrochloric acid upon the silver salt), it is stable even when boiled with dilute acids or alkalis. The solution is colourless and has a strongly acid reaction. In the course of time, however, the aqueous solution also decomposes into nitrous oxide and water. The complete oxidation by permanganate of potash proceeds according to the following equation: $5\text{H}_2\text{N}_2\text{O}_2 + 8\text{KMnO}_4 + 12\text{H}_2\text{SO}_4 = 10\text{HNO}_3 + 4\text{K}_2\text{SO}_4 + 8\text{MnSO}_4 + 12\text{H}_2\text{O}$. In alkaline solution, KMnO_4 only oxidises hyponitrous acid into nitrous and not into nitric acid. Nitrous acid has a decomposing action upon hyponitrous acid, and if the aqueous solutions of the two acids be mixed together they immediately give off oxides of nitrogen. Hyponitrous acid does not liberate CO_2 from its salts, but, on the other hand, it is not displaced by CO_2 .

of certain metals—for instance, of zinc ⁶⁸—gives nitrous oxide, although in this case mixed with nitric oxide. The usual method of preparing nitrous oxide consists in the decomposition of ammonium nitrate by the aid of heat, because in this case only water and nitrous oxide are formed, $\text{NH}_4\text{NO}_3 = 2\text{H}_2\text{O} + \text{N}_2\text{O}$ (a mixture of NH_4Cl and KNO_3 is sometimes taken). The decomposition ⁶⁹ proceeds very easily in an apparatus like that used for the preparation of ammonia or oxygen—that is, in a retort or flask with a gas-conducting tube. The decomposition must, however, be carried on carefully, as otherwise nitrogen is formed from the decomposition of the nitrous oxide.⁷⁰

Nitrous oxide is a colourless gas with a faint but characteristic smell. It is somewhat soluble in cold water, but only slightly soluble in warm water (and is therefore collected over warm water). It is not a permanent gas (absolute boiling-point $+39^\circ$), that is, it is easily liquefied by the action of cold under a high pressure; at 15° it may be liquefied by a pressure of about 40 atmospheres. The gas is usually liquefied by means of the force pump ⁷¹ shown in fig. 59. As it is liquefied with comparative ease, and as the cold produced by its vaporisation is very considerable,⁷² it is often employed (as also is liquid carbonic anhydride) in investigations requiring a low temperature.

⁶⁸ It is remarkable that electro-deposited copper powder gives nitrous oxide with a 10 per cent. solution of nitric acid, whilst ordinary copper gives nitric oxide. It is here evident that the physical and mechanical structure of the substance affects the course of the reaction—that is to say, it is a case of contact or surface action.

⁶⁹ This decomposition is accompanied by the evolution of about 25,000 calories per gram-molecule, NH_4NO_3 , and therefore takes place with ease, and sometimes with an explosion.

⁷⁰ In order to remove any nitric oxide that might be present, the gas obtained is passed through a solution of ferrous sulphate. As nitrous oxide is very soluble in cold water (at 0° , 100 volumes of water dissolve 130 volumes of N_2O ; at 20° , 67 volumes), it must be collected over warm water. The nitrous oxide is much more soluble than nitric oxide, which is in agreement with the fact that nitrous oxide is much more easily liquefied than nitric oxide. Villard obtained a crystallohydrate, $\text{N}_2\text{O} \cdot 6\text{H}_2\text{O}$, which was tolerably stable at 0° .

⁷¹ Faraday obtained liquid nitrous oxide by the same method as he employed for liquid ammonia, by heating dry ammonium nitrate in a closed bent tube, one arm of which was immersed in a freezing mixture. In this case two layers of liquid are obtained at the cooled end, a lower layer of water and an upper layer of nitrous oxide. This experiment should be conducted with great care, as the pressure of the nitrous oxide in a liquid state is considerable, namely (according to Regnault), at $+10^\circ$, 45 atmospheres, at 0° , 36 atmospheres, at -10° , 29 atmospheres, and at -20° , 23 atmospheres. It boils at about -90° , and the pressure is then of course 1 atmosphere.

⁷² Liquid nitrous oxide, in vapourising at the same pressures as liquid carbonic anhydride, gives rises to almost equal or even slightly lower temperatures. Thus at a pressure of 25 mm. carbonic anhydride gives a temperature as low as -115° , and nitrous oxide -125° (Dewar). The similarity of these properties and even of the absolute boiling-point ($\text{CO}_2 + 32^\circ$, $\text{N}_2\text{O} + 36^\circ$) is all the more remarkable because these gases have the same molecular weight, namely, 44.

Liquid nitrous oxide is a very mobile, colourless liquid, which boils at -89.8° , acts on the skin, and is incapable of oxidising potassium, phosphorus, or carbon; its specific gravity is slightly less than that of water (0.910 at 0° , 0.856 at 10° , 0.60 at 35° , and 0.45 at

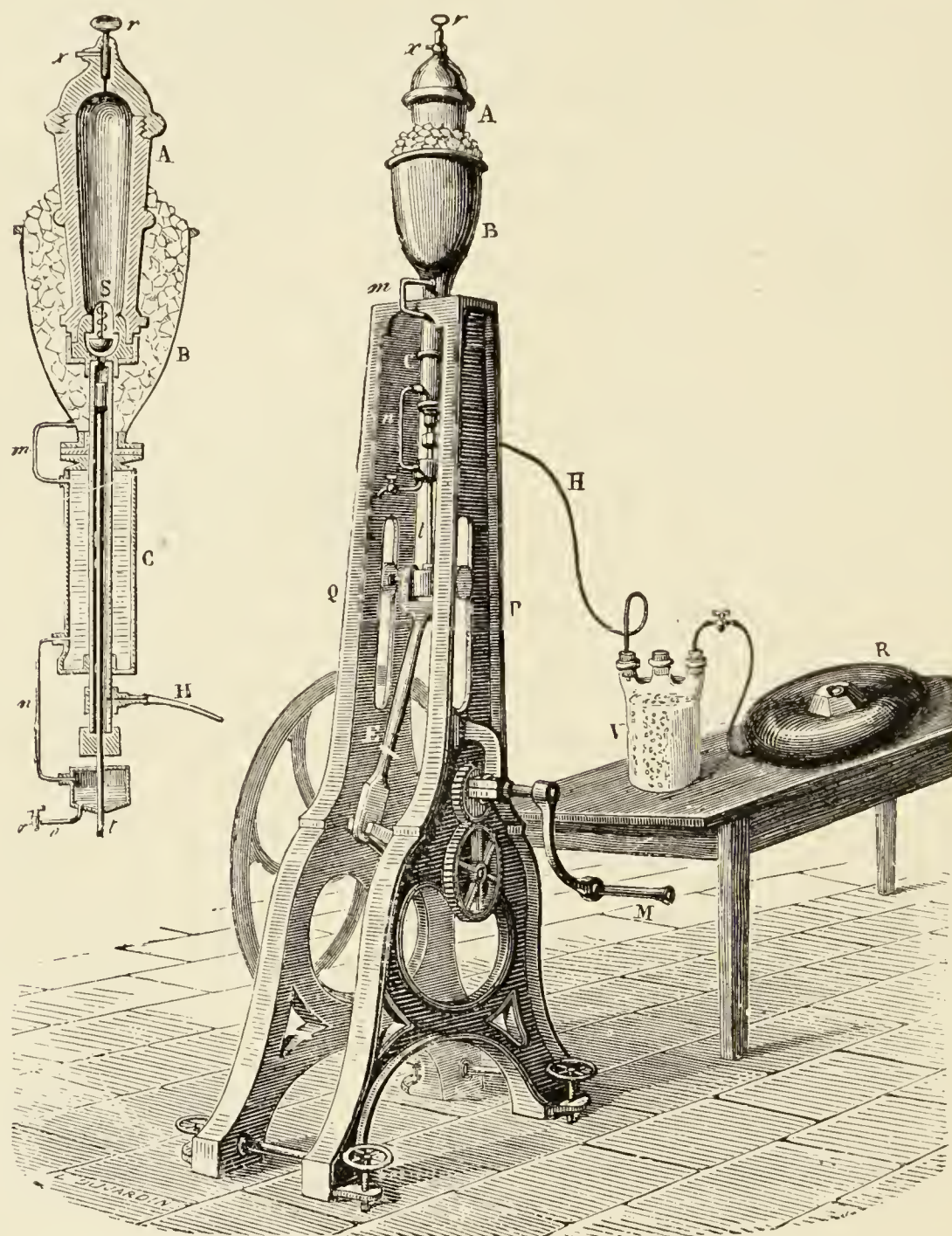


FIG. 59.—Natterer's apparatus for the preparation of liquid nitrous oxide and carbonic anhydride. The gas first passes through the vessel V, for drying, and then into the pump (a section of the upper part of the apparatus is given on the left). The piston *t* of the force pump is moved by the crank E and fly-wheel turned by hand. The gas is pumped into the iron chamber A, where it is liquefied. The valve S allows the gas to enter A, but not to escape from it. The chamber and pump are cooled by the jacket B, filled with ice. When the gas is liquefied the vessel A is unscrewed from the pump, and the liquid may be poured from it by inverting it and unscrewing the valve *r*, when the liquid runs out of the tube *x*.

39° ; Villard, 1894). When it is evaporated under the receiver of an air-pump, its temperature falls to -100° , and the liquid solidifies into a snowlike mass, and partially forms transparent crystals. Both these substances are solid nitrous oxide. It melts at about -102° .⁷³

⁷³ A very characteristic experiment of simultaneous combustion and intense cold may be performed by means of liquid nitrous oxide; if liquid nitrous oxide be poured

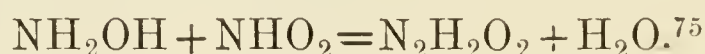
When introduced into the respiratory organs (and consequently, owing also to its solubility, in the blood) nitrous oxide produces a peculiar kind of intoxication accompanied by spasmodic movements, and hence this gas, discovered by Priestley in 1776, received the name of *laughing gas*. On prolonged respiration it produces a state of insensibility (it is an anæsthetic like chloroform), and is therefore employed in dental and surgical operations, but too prolonged respiration causes death.

Nitrous oxide is easily decomposed into nitrogen and oxygen by the action either of heat, or of a series of electric sparks; and this explains why a number of substances which cannot burn in nitric oxide do so with great ease in nitrous oxide. In fact, when nitric oxide yields oxygen on decomposition, it immediately absorbs it, forming NO_2 ; whilst nitrous oxide does not possess this capacity for further combination with oxygen.⁷⁴ A mixture of nitrous oxide with hydrogen explodes like detonating gas, gaseous nitrogen being formed, $\text{N}_2\text{O} + \text{H}_2 = \text{H}_2\text{O} + \text{N}_2$. The volume of the remaining nitrogen is equal to that of the original nitrous oxide, and also to that of the hydrogen entering into combination with the oxygen; hence in this reaction equal volumes of nitrogen and hydrogen replace each other. Nitrous oxide is also very easily decomposed by red-hot metals; also sulphur, phosphorus, and charcoal burn in it, although not so brilliantly as in oxygen. A substance in burning in nitrous oxide evolves more heat than an equal quantity burning in oxygen; which clearly shows that in the formation of nitrous oxide by the combination of nitrogen with oxygen there is not an evolution but an absorption of heat, there being no other source for the excess of heat in the combustion of substances in nitrous oxide (see note 28). If a given volume of nitrous oxide be decomposed by a metal—for instance sodium—there remains, after cooling, a volume of nitrogen exactly equal to that of the nitrous oxide taken; consequently the oxygen is, as it were, distributed between the atoms of nitrogen without producing an increase in the volume of the nitrogen.

into a test tube containing mercury the latter will solidify, and if a piece of red-hot charcoal be thrown upon the surface of the nitrous oxide it will continue to burn very brilliantly, giving rise to a high temperature.

⁷⁴ In the following chapter we shall consider the volumetric composition of the oxides of nitrogen, which will explain the difference between nitric and nitrous oxides. Nitrous oxide is formed with a diminution of volume (contraction), but nitric oxide without contraction, its volume being equal to the sum of the volumes of the nitrogen and oxygen of which it is composed. By oxidation, if this could be directly accomplished, two volumes of nitrous oxide and one volume of oxygen would not give three but four volumes of nitric oxide. These facts must be taken into consideration in comparing the heats of formation, the capacities for supporting combustion, and other properties of nitrous and nitric oxides, N_2O and NO .

Although nitrous oxide, N_2O , is not absorbed by caustic alkalies, for instance, NaHO , nor by basic oxides, for instance, PbH_2O_2 , yet saline compounds such as N_2NaHO_2 or PbN_2O_2 and their corresponding **hyponitrous acid**, $\text{N}_2\text{H}_2\text{O}_2$, forming as it were the hydrate of nitrous oxide, are known and are formed in the decomposition of nitrous oxide (see note 67). The salts of hyponitrous acid are best formed by the reduction (by sodium amalgam, hydrated ferrous oxide, &c.) of the salts of nitrous acid, or by their double decomposition with the salts of hydroxylamine.



⁷⁵ It is said that a peculiar isomeride of hyponitrous acid— $\text{N}_2\text{H}_2\text{O}_2$ —is obtained from nitrourethane, $\text{C}_3\text{H}_6\text{N}_2\text{O}_4$, but this question is not sufficiently certain to be treated of in an elementary text-book.

CHAPTER VII

MOLECULES AND ATOMS. THE LAWS OF GAY-LUSSAC AND AVOGADRO-GERHARDT.

HYDROGEN combines with oxygen in the proportion of two volumes to one. The composition by volume of nitrous oxide is exactly similar—this gas being composed of two volumes of nitrogen and one volume of oxygen. By decomposing ammonia by the action of an electric spark it is easy to prove that it contains one volume of nitrogen to three volumes of hydrogen. So, similarly, whenever a compound is decomposed and the **volumes of the gases** proceeding from it are measured, it is found that the volumes of the gases or vapours entering into combination stand in very simple relations to one another. With water, nitrous oxide, &c., this may be proved by direct observation; but in the majority of cases, and especially with substances which, although volatile—that is, capable of passing into a gaseous (or vaporous) state—are liquid at the ordinary temperature, such a direct method of observation presents many difficulties. But, then, if the densities of the vapours and gases be known, the same simplicity in their ratio is shown by calculation. The volume of a substance is proportional to its weight, and inversely proportional to its density, and therefore by dividing the amount by weight of each substance entering into the composition of a compound by its density in the gaseous or vaporous state we shall obtain factors which will be in the same proportion as the volumes of the substances entering into the composition of the compound.¹ Thus, for example, water contains eight parts by weight of oxygen to one part by weight of hydrogen, and their densities are 16

¹ If the weight be indicated by P, the density by D, and the volume by V, then

$$\frac{P}{D} = KV$$

where K is a coefficient depending on the method of expressing P, D, and V. But, whatever it be, K is cancelled in dealing with the comparison of volumes, because comparative and not absolute measures of volumes are taken. In this chapter, as throughout the book, the weight P is given in grams in dealing with absolute weights; and if comparative, as in the expression of chemical composition, then the weight of an atom of oxygen is taken as 16, and that of an atom of hydrogen as 1.008.

and 1; consequently their volumes (or the above-mentioned factors) are 1 and $\frac{1}{2}$, and therefore it is seen without direct experiment that water contains two volumes of hydrogen for every one volume of oxygen. So also, knowing that nitric oxide contains fourteen parts of nitrogen and sixteen parts of oxygen, and knowing that the specific gravities of these last two gases are fourteen and sixteen, we see that the volumes in which nitrogen and oxygen combine for the formation of nitric oxide are in the proportion of 1 : 1. We will cite another example. In the last chapter we saw that the density of NO_2 only becomes constant and equal to twenty-three (referred to hydrogen) above 135° , and as a matter of fact a method of direct observation of the volumetric composition of this substance would be very difficult at so high a temperature. But it may be easily calculated. NO_2 , as is seen from its formula and analysis, contains thirty-two parts by weight of oxygen and fourteen parts by weight of nitrogen, forming forty-six parts by weight of NO_2 , and knowing the densities of these gases we find that one volume of nitrogen with two volumes of oxygen gives two volumes of nitrogen peroxide. Therefore, knowing the amounts by weight of the substances participating in a reaction or forming a given substance, and knowing the densities of the gases or vapours,² the

² As the volumetric relations of vapours and gases, next to the relations of substances by weight, form the most important province of chemistry, and a very important means for the attainment of chemical conclusions, and as, further, these volumetric relations are determined by the densities of gases and vapours, the **methods of determining the densities** of vapours (and also of gases) are necessarily important factors in chemical research. These methods are described in detail in works on physics and physical and analytical chemistry, and therefore we here only touch on the general principles involved.

If we know the weight p of the vapour of a given substance and the volume v , occupied by it at a temperature t and pressure h , its density may be directly obtained by dividing p by the weight of a volume v of hydrogen (if the density be expressed relatively to that of hydrogen, see Chapter II., note 23) at t and h . Hence the methods of determining the densities of vapours and gases are based on the determination of p , v , t , and h . The last two data (the temperature t and pressure h) are given by the thermometer and barometer and the heights of mercury or other liquid confining the gas, and therefore do not require further explanation. It need only be remarked that: (1) In the case of readily volatile liquids there is no difficulty in procuring a bath with a constant temperature, but that it is nevertheless best (especially considering the inaccuracy of thermometers) to have a medium of absolutely constant temperature, and therefore to take either a bath in which some substance is melting—such as one of melting ice at 0° or one of crystals of sodium acetate, melting at $+56^\circ$ —or, as is more generally practised, to place the vessel containing the substance to be experimented with in the vapour of a liquid boiling at a definite temperature, and knowing the pressure under which it is boiling, to determine the temperature of the vapour. For this purpose the boiling-points of water at different pressures are given in Chapter I., note 11, and the boiling-points of certain easily procurable liquids at various pressures are given in Chapter II., note 27. (2) With respect to temperatures above 300° these are most simply obtained constant (to give time for the volume of a substance being observed, and to allow it to attain the calculated temperature t) by means of substances boiling at a high temperature. Thus, for instance, at the

volumetric relations of the substances taking part in a reaction or entering into the composition of a compound, may also be determined.

ordinary atmospheric pressure the temperature t of the vapour of *sulphur* is about 445° , of phosphorus pentasulphide 518° , of tin chloride 606° , of cadmium 770° , of zinc 930° (according to Violle and others), or 1040° (according to Deville), &c. (3) The indications of the thermometer must be corrected in the manner described in text-books of physics. (4) The temperature of the vapour used as the bath should in every case be several degrees higher than the boiling-point of the liquid whose density is to be determined, in order that no portion may remain in a liquid state. But even in this case, as is seen from the example of nitric peroxide (Chapter VI.), the vapour density does not always remain constant with a change of t , as it should do were the law of the expansion of gases and vapours absolutely exact (Chapter II., note 25). If variations of a chemical and physical nature, similar to that which we saw in nitric peroxide, take place in the vapours,

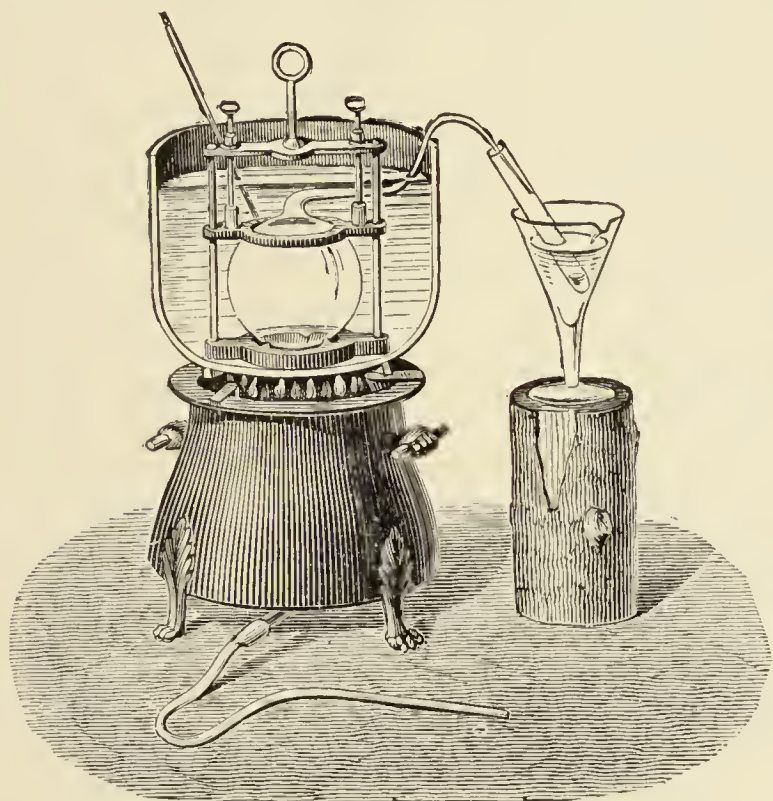


FIG. 60.—Apparatus for determining the vapour density by Dumas' method. A small quantity of the liquid whose vapour density is to be determined is placed in the glass globe, and heated in a water or oil bath to a temperature above the boiling-point of the liquid. When all the liquid has been converted into vapour and has displaced all the air from the globe, the latter is sealed up and weighed. The capacity of the globe is then measured, and in this manner the volume occupied by a known weight of vapour at a known temperature is determined.

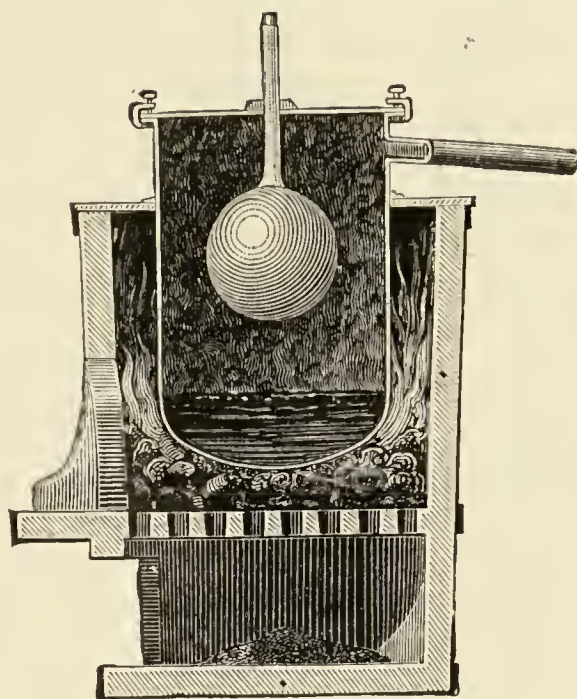


FIG. 61.—Deville and Troost's apparatus for determining the vapour densities by Dumas' method, of substances which boil at high temperatures. A porcelain globe containing the substance whose vapour density is to be determined is heated in the vapour of mercury (350°), sulphur (410°), cadmium (850°), or zinc (1040°). The globe is sealed up in an oxyhydrogen flame.

the main interest is centred in *constant* densities, which do not vary with t , and therefore the possible effect of t on the density must always be kept in mind in having recourse to this means of investigation. (5) Usually, for the sake of convenience of observation, the vapour density is determined at the atmospheric pressure, which is read on the barometer; but in the case of substances which are volatilised with difficulty, and also of substances which decompose, or, in general, vary at temperatures near their boiling-points, it is best or even indispensable to conduct the determination at low pressures; whilst for substances which decompose at low pressures the observations have to be conducted under a more or less considerably increased pressure. (6) In many cases it is convenient to determine the vapour density of a substance in admixture with other gases, and consequently under a partial pressure, which may be calculated from the volume of the mixture and that of the intermixed gas (see Chap. I., note 1). This method is especially important for substances which are easily decomposable, because, as shown by the phenomena of

Such an investigation (either direct or by calculation from the densities and composition) of every chemical reaction resulting in the formation of a substance is able to remain unchanged in the atmosphere of one of its products of decomposition. Thus, Wurtz determined the density of phosphoric

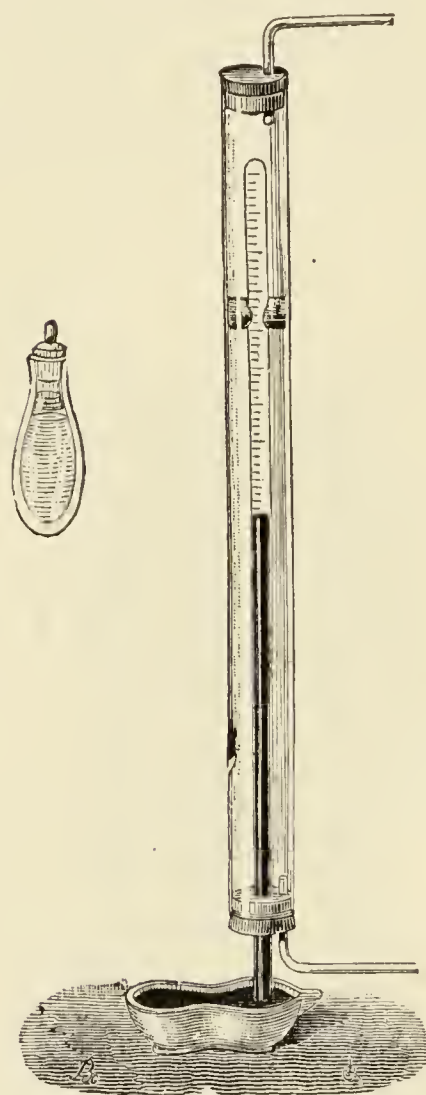


FIG. 62.—Hofmann's apparatus for determining vapour densities. The internal tube, which is about one metre long, and is calibrated and graduated, is filled with mercury and inverted in a mercury bath. A small bottle (depicted in its natural size on the left) containing a weighed quantity of the liquid whose vapour density is to be determined, is introduced into the Torricellian vacuum. Steam, or the vapour of amyl alcohol, &c., is passed through the outer tube, and heats the internal tube to the temperature t , at which the volume of vapour is measured.

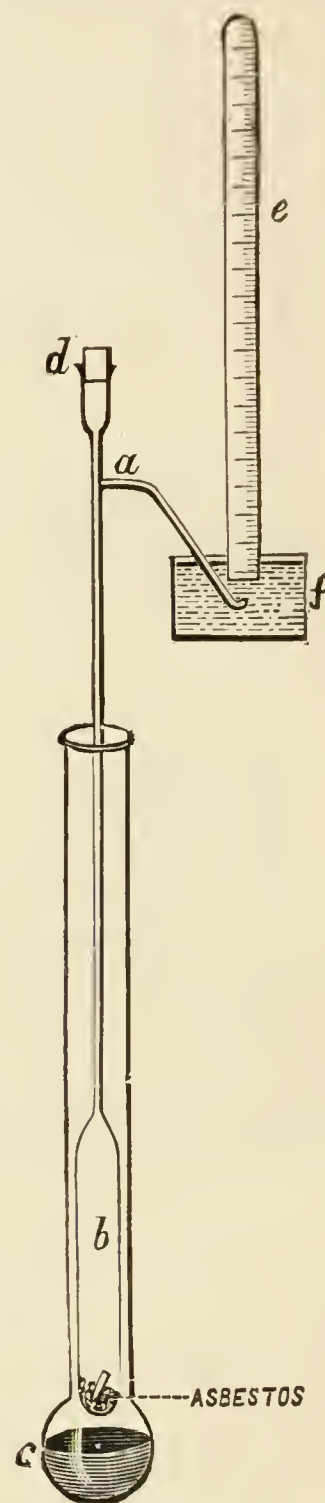


FIG. 63.—Victor Meyer's apparatus for determining vapour densities. The tube b is heated in the vapour of a liquid of constant boiling-point. A glass tube, containing the liquid to be experimented upon, is caused to fall from d . The air displaced is collected in the cylinder e , in the trough f .

chloride, PCl_5 , in admixture with the vapour of phosphorous chloride, PCl_3 . If the relative density does not vary with the pressure and temperature (at least, to an extent appreciably exceeding the limits of experimental error), then this *constant* density indicates the *gaseous* and *invariable* state of a substance. The laws hereafter laid down refer only to such vapour densities. But the majority of volatile substances show such a constant density at a certain degree above their boiling-points up to the

tion of definite chemical compounds, shows that the volumes of the reacting substances in a gaseous or vaporous state are either equal or are in simple multiple proportion.³ This forms the **first law** of those discovered

starting-point of decomposition. Thus, the density of aqueous vapour hardly varies from the ordinary temperature up to 1000° (there are no trustworthy determinations beyond this) and for pressures varying from fractions of an atmosphere up to several atmospheres. If, however, the density does vary considerably with a variation of p and t , it may serve as a guide for the investigation of the chemical changes which are undergone by the substance in a state of vapour, or at least as an indication of a deviation from the laws of Boyle-Mariotte and Gay-Lussac (for the expansion of gases with t). In certain cases the separation of one form of deviation from the other may be explained by special hypotheses.

With respect to the means of determining p and v , with a view to finding the vapour density, we may distinguish three chief methods: (*a*) by weight, that is, by ascertaining the weight of a definite volume of vapour; (*b*) by volume, that is, by measuring the volume occupied by the vapour of a definite weight of a substance; and (*c*) by displacement. The last mentioned is essentially volumetric, because a known weight of a substance is taken, and the volume of the air displaced by the vapour at a given t and p is determined.

The method by weight (*a*) is the most trustworthy and historically important. **Dumas' method** is typical. An ordinary spherical glass or porcelain vessel, like those shown respectively in figs. 60 and 61, is taken, and an excess of the substance to be experimented upon is introduced into it. The vessel is heated to a temperature t° , higher than the boiling-point of the liquid; this gives a vapour which displaces the air, and fills the spherical space. When the air and vapour cease escaping from the sphere, the latter is fused up or closed by some means; and when cool, the weight of the vapour remaining in the sphere is determined (either by direct weighing of the vessel with the vapour and introducing the necessary corrections for the weight of the air and of the vapour itself, or by determining the weight of the volatilised substance by chemical methods), and the volume of the vapour at t and the barometric pressure h are then calculated.

The volumetric method (*b*) originally employed by Gay-Lussac and then modified by Hofmann and others is based on the principle that a weighed quantity of the liquid to be experimented with (placed in a small closed vessel, which is sometimes fused up before weighing, and, if quite full of the liquid, breaks when heated in a vacuum) is introduced into a graduated cylinder heated to t , or simply into a Torricellian vacuum, as shown in fig. 62, and the number of volumes occupied by the vapour noted when the space holding it is heated to the desired temperature t .

The method of displacement (*c*) proposed by Victor Meyer is based on the fact that a space b is heated to a constant temperature t (by the surrounding vapours of a liquid of constant boiling-point), and the air (or other gas enclosed in this space) is allowed to attain this temperature, and when it has done so a glass bulb containing a weighed quantity of the substance to be experimented with is dropped into the space. The substance is immediately converted into vapour, and displaces the air into the graduated cylinder c . The amount of this air is calculated from its volume, and hence the volume at t° , and therefore also the volume occupied by the vapour, is found. The general arrangement of the apparatus is given in fig. 63.

³ Vapours and gases, as already explained in the second chapter, are subject to the same laws, which are, however, only approximate. It is evident that for the deduction of the laws which will presently be enunciated it is only possible to take into consideration a perfect gaseous state (far removed from the liquid state) and chemical invariability in which the *vapour density is constant*—that is, the volume of a given gas or vapour varies, like a volume of hydrogen, air, or other gas, with the pressure and temperature.

It is necessary to make this statement in order that it may be clearly seen that the laws of gaseous volumes, which we shall describe presently, are in the most intimate connection with the laws of the variation of volume with pressure and temperature. And as these latter laws (Chap. II.) are not infallible but only approximately exact, the

by **Gay-Lussac**. It may be formulated as follows: *The amounts of substances entering into chemical reaction occupy under similar physical conditions, in a gaseous or vaporous state, equal or simple multiple volumes.* This law refers, not only to elements, but also to compounds entering into chemical combination. Thus, for example, one volume of ammonia gas combines with one volume of hydrogen chloride; for in the formation of sal-ammoniac, NH_4Cl , there enter into reaction 17 parts by weight of ammonia, NH_3 , which is 8.5 times denser than hydrogen, and 36.5 parts by weight of hydrogen chloride, whose vapour density is 18.25 times that of hydrogen, as has been proved by direct experiment. By dividing the weights by the respective densities we find that the volume of ammonia, NH_3 , is equal to two, and so also is the volume of hydrogen chloride. Hence the volumes of the compounds which here combine are equal. Taking into consideration that the law of Gay-Lussac holds good, not only for elements, but also for compounds, it should be expressed as follows: **Substances interact with one another in commensurable volumes of their vapours.**⁴

The law of combining volumes and the law of multiple proportion were discovered independently of each other—the one in France by Gay-Lussac, the other in England by Dalton—almost simultaneously. In the language of the atomic hypothesis it may be said that atomic quantities of elements occupy in the gaseous state equal or multiple volumes.

The first law of Gay-Lussac expresses the relation between the volumes of the component parts of a compound. Let us now consider the relation existing between the volumes of the component parts and those of the compounds which proceed from them. This may sometimes be determined by direct observation. Thus the volume occupied by water, formed by two volumes of hydrogen and one volume of oxygen, may be determined by the aid of the apparatus shown in fig. 64. The long same is the case with the laws about to be described. And as it is possible to find more exact laws (a second approximation) for the variation of v with p and t (for example, van der Waals' formula, Chap. II., note 33), so also a more exact expression of the relation between the composition and the density of vapours and gases is possible. But to prevent any doubt arising at the very beginning as to the extent and general application of the laws of volumes, it will be sufficient to mention that the densities of such gases as oxygen, nitrogen, and carbonic anhydride are already known to *remain constant* (within the limits of experimental error) between the ordinary temperature and a white heat; whilst, judging from what is said in my work on the 'Pressure of Gases' (vol. i., p. 9), it may be said that, as regards pressure, the relative density remains very constant, even when the deviations from Mariotte's law are very considerable. However, in this respect the number of data is as yet too small to allow of an exact conclusion.

⁴ We must recollect that this law is only approximate, like Boyle and Mariotte's law, and that, therefore, like the latter, a more exact expression may be found for the exceptions.

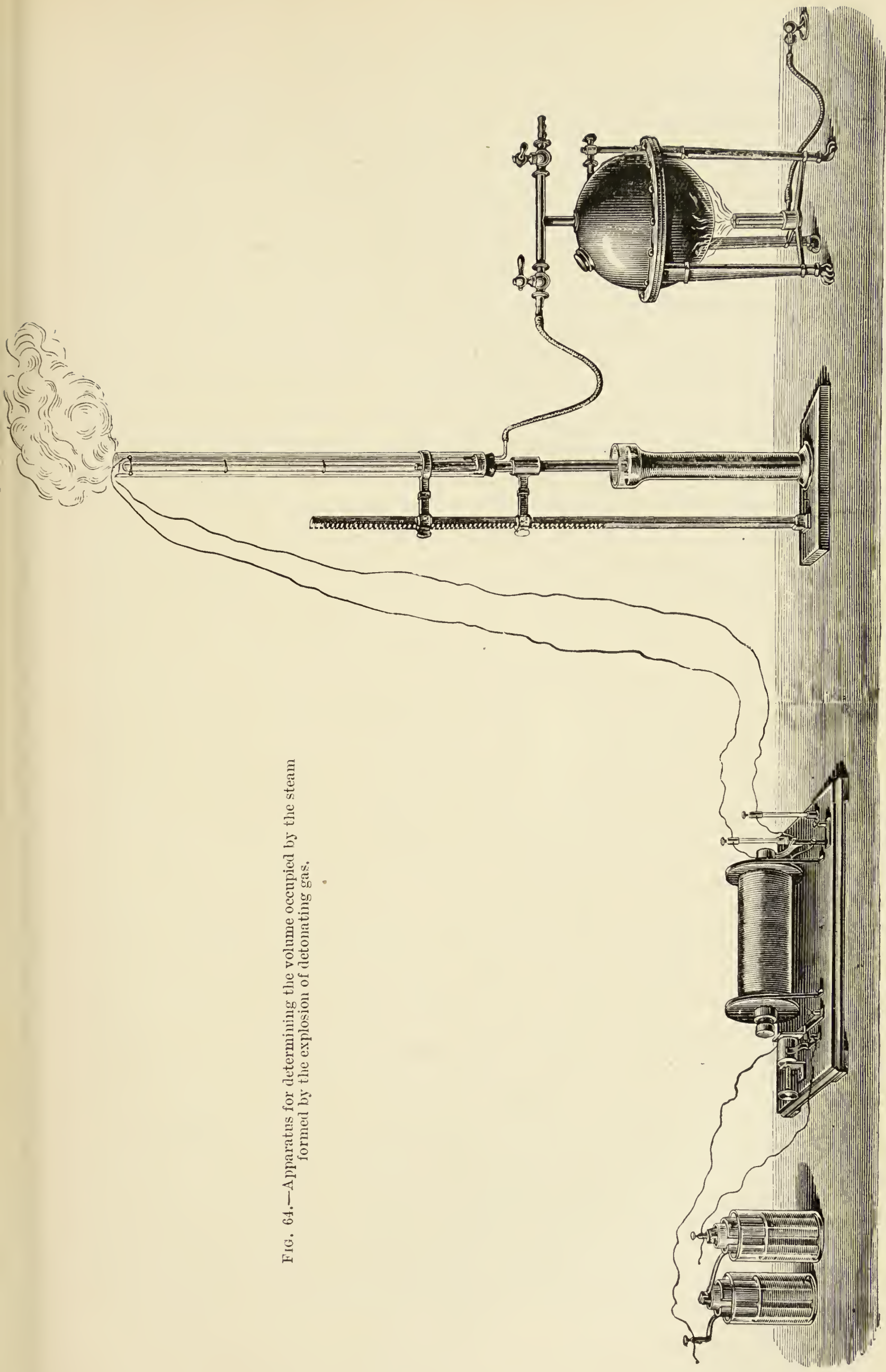


FIG. 64.—Apparatus for determining the volume occupied by the steam formed by the explosion of detonating gas.

glass tube is closed at the top and open at the bottom, which is immersed in a cylinder containing mercury. The closed end is furnished with wires like a eudiometer. The tube is filled with mercury, and then a certain volume of detonating gas is introduced. This gas is obtained from the decomposition of water, and therefore, in every three volumes, contains two volumes of hydrogen and one volume of oxygen. The tube is surrounded by a second and wider glass tube, and the vapour of a substance boiling above 100° —that is, whose boiling-point is higher than that of water—is passed through the annular space between them. Amyl alcohol, whose boiling-point is 132° , may be taken for this purpose. The amyl alcohol is boiled in the vessel to the right hand and its vapour passed between the walls of the two tubes. In the case of amyl alcohol the outer glass tube should be connected with a condenser to prevent the escape into the air of the unpleasant-smelling vapour. The detonating gas is thus heated up to a temperature of 132° . When its volume becomes constant it is measured, the height of the column of mercury in the tube above the level of the mercury in the cylinder being noted. Let this volume equal v ; it will therefore contain $\frac{1}{3}v$ of oxygen and $\frac{2}{3}v$ of hydrogen. The current of vapour is then stopped and the gas exploded; water is formed, which condenses into a liquid. The volume occupied by the vapour of the water formed has now to be determined. For this purpose the vapour of the amyl alcohol is again passed between the tubes, and thus the whole of the water formed is converted into vapour at the same temperature as that at which the detonating gas was measured; and the cylinder of mercury being raised until the column of mercury in the tube stands at the same height above the surface of the mercury in the cylinder as it did before the explosion, it is found that the volume of the water formed is equal to $\frac{2}{3}v$, that is, it is equal to the volume of the hydrogen contained in it. Consequently the volumetric composition of water is expressed in the following terms: Two volumes of hydrogen combine with one volume of oxygen to form two volumes of aqueous vapour. For substances which are gaseous at the ordinary temperature this direct method of observation is sometimes very easily carried out; for instance, with ammonia and with nitric and nitrous oxides. Thus to determine the composition by volume of nitrous oxide, the above-described apparatus may be employed. Nitrous oxide is introduced into the tube, and, after measuring its volume, electric sparks are passed through the gas; it is then found that two volumes of nitrous oxide have given three volumes of gases—namely, two volumes of nitrogen and one volume of oxygen. Consequently the composition of nitrous oxide is similar to that of water; two volumes of nitrogen and one

volume of oxygen give two volumes of nitrous oxide. By decomposing ammonia it is found to be composed in such a manner that two volumes of it give one volume of nitrogen and three volumes of hydrogen; also two volumes of nitric oxide are formed by the union of one volume of oxygen with one volume of nitrogen. The same relations may be proved by calculation from the vapour densities, as was described above.

Comparisons of various results made by the aid of direct observations or calculation, an example of which has just been cited, led Gay-Lussac to the conclusion that *the volume of a compound in a gaseous or vaporous state is always in simple multiple proportion to the volume of each of the component parts of which it is formed* (and consequently to the sum of the volumes of the elements of which it is formed). This is the **second law of Gay-Lussac**; it extends the simplicity of the volumetric relations to compounds, and is of the same nature as that presented by the elements entering into mutual combination. Hence not only the substances forming a given compound, but also the substances formed, exhibit a simple relation of volume when measured as vapour or gas.⁵

When a compound is formed from two or more components, there may or may not be a contraction; the volume of the reacting substances is in this case either equal to or greater than the volume of the resultant compound. The reverse is naturally observed in the case of decompositions, when from one substance there are produced several of simpler nature. Therefore in the future we shall term **combination** a reaction in which a contraction is observed—that is, a diminution in the volume of the component bodies in a state of vapour or gas; and we shall term **decomposition** a reaction in which an expansion is produced; while those reactions in which the volumes in a gaseous or vaporous state remain constant (the volumes being naturally compared at the same temperature and pressure) we shall term reactions of **substitution** or of double decomposition. Thus the transition of oxygen into ozone is a reaction of combination, the formation of nitrous oxide from oxygen and nitrogen will also be a combination, the formation of nitric oxide from the same will be a reaction of

⁵ This second law of volumes may be considered as a consequence of the first law. The first law requires simple ratios between the volumes of the combining substances *A* and *B*. A substance *AB* is produced by their combination. It may, according to the law of multiple proportion, combine, not only with substances *C*, *D*, &c., but also with *A* and with *B*. In this new combination the volume of *AB*, combining with the volume of *A*, should be in simple multiple proportion with the volume of *A*; hence the volume of the compound *AB* is in simple proportion to the volume of its component parts. Therefore only one law of volumes need be accepted. We shall afterwards see that the third law of volumes (Avogadro-Gerhardt) also embraces the first two laws.

substitution, the action of oxygen on nitric oxide a combination, and so on.

The amount of contraction produced in the formation of chemical compounds not infrequently leads to the possibility of distinguishing the degree of change which takes place in the chemical character of the components when combined. In those cases in which a contraction occurs, the properties of the resultant compounds are very different from the properties of the substances of which it is composed. Thus ammonia bears no resemblance in its physical or chemical properties to the elements from which it is derived; a contraction takes place in a state of vapour (two volumes of ammonia being formed from three volumes of hydrogen and one volume of nitrogen), indicating a proximation of the elements—the distance between the atoms is diminished, and from gaseous substances there is formed a liquid substance, or at any rate one which is easily liquefied. For this reason nitrous oxide, formed by the condensation of two permanent gases, is a substance which is somewhat easily converted into a liquid; again, nitric acid, which is formed from elements which are permanent gases, is a liquid, whilst, on the contrary, nitric oxide, which is formed without contraction and is decomposed without expansion, remains a gas which is as difficult to liquefy as nitrogen and oxygen. In order to obtain a still more complete idea of the dependence of the properties of a compound on the properties of the component substances, it is further necessary to know the quantity of heat which is developed in the formation of the compound. If this quantity be large—as, for example, in the formation of water—then the amount of energy in the resultant compound will be considerably less than the energy of the elements entering into its composition; whilst, on the contrary, if the amount of heat evolved in the formation of a compound be small, or if there be an absorption of heat, as in the formation of nitrous oxide, the energy of the elements is not destroyed, or is only altered to a slight extent; hence, notwithstanding the contraction (compression) involved in its formation, nitrous oxide supports combustion.

The preceding laws were deduced from purely experimental and empirical data, and as such evoke further consequences, as the law of multiple proportions gave rise to the atomic theory and to the law of equivalents (Chapter IV.). In view of the atomic conception of the constitution of substances, the question naturally arises as to what, then, are the relative volumes proper to those physically indivisible molecules which chemically react on each other and consist of the atoms of elements. The simplest possible hypothesis in this respect would be that the volumes of the molecules of substances are equal; or,

what is the same thing, to suppose that equal volumes of vapours and gases contain an equal number of molecules. This proposition was first enunciated by the Italian savant **Avogadro** in 1810. It was also admitted by the French physico-mathematician **Ampère** (1815) for the sake of simplifying all kinds of physico-mathematical conceptions respecting gases. But Avogadro and Ampère's propositions were not generally received in science until after **Gerhardt** in the forties had applied them to the generalisation of chemical reactions, and had demonstrated, by aid of a series of phenomena, that the reactions of substances actually take place with the greatest simplicity, and more especially that such reactions take place between those quantities of substances which occupy equal volumes, and until he had stated the hypothesis in an exact manner and deduced the consequences that necessarily follow from it. Following Gerhardt, Clausius, in the fifties, placed this hypothesis of the equality of the numbers of molecules in equal volumes of gases and vapours on the basis of the kinetic theory of gases. At the present day the hypothesis of Avogadro and Gerhardt lies at the basis of contemporary physical, mechanical, and chemical conceptions; the consequences arising from it have often been subject to doubt, but in the end have been verified by the most diverse methods; and now, when all efforts to refute those consequences have proved fruitless, the hypothesis must be considered as verified,⁶ and the **law of Avogadro-Gerhardt** must be spoken of as fundamental, and as of great importance for the comprehension of the phenomena of nature. The law may now be formulated from two points of view. In the first place, from a physical aspect, **equal volumes of gases** (or vapours) at the same temperature and pressure **contain the same number of molecules**—or of particles of matter which are neither mechanically nor physically divisible—previous to chemical change. In the second place, from a chemical aspect, the same law may be expressed thus: **the quantities of substances entering into chemical reactions occupy, in a state of vapour or gas, equal volumes**. For our purpose, the chemical aspect is the more important, and therefore, before developing the law and its consequences, we will consider the chemical phenomena from which the law is deduced or which it serves to explain.

⁶ It must not be forgotten that Newton's law of gravity was first an hypothesis, but it became a trustworthy, perfect theory, and acquired the qualities of a fundamental law owing to the concord between its deductions and actual facts. All laws, all theories, of natural phenomena are at first hypotheses. Some are rapidly established by their consequences exactly agreeing with facts, others only take root by slow degrees; and there are many which are refuted owing to their consequences being found to be at variance with facts; while others are retained only because of their possibility and of some convenience or other in their application, but not permanently unless their consequences can be verified in their different aspects and completely.

When two isolated substances interact with each other directly and easily, it is found that the reaction is accomplished between quantities which in a gaseous state occupy equal volumes. Thus ammonia, NH_3 , reacts directly with hydrochloric acid, HCl , forming sal-ammoniac, NH_4Cl , and in this case the 17 parts by weight of ammonia occupy the same volume as the 36.5 parts by weight of hydrochloric acid.⁷ Ethylene, C_2H_4 , combines with chlorine, Cl_2 , in only one proportion, forming ethylene dichloride, $\text{C}_2\text{H}_4\text{Cl}_2$, and this combination proceeds directly and with great facility, the reacting quantities occupying equal volumes. Chlorine reacts with hydrogen in only one proportion, forming hydrochloric acid, HCl , and in this case equal volumes interact with each other. An equality of volumes is also observed in cases of decomposition, taking place in substances which split up into two others. Indeed, acetic acid breaks up into marsh gas, CH_4 , and carbonic anhydride, CO_2 , and in the proportions in which they are formed from acetic acid they occupy equal volumes. From phthalic acid, $\text{C}_8\text{H}_6\text{O}_4$, there may be obtained benzoic acid, $\text{C}_7\text{H}_6\text{O}_2$, and carbonic anhydride, CO_2 , and as all the elements of phthalic acid enter into the composition of these substances, it follows that, although they cannot re-form it by their direct action on each other (the reaction is not reversible), still they form the direct products of its decomposition, and they occupy equal volumes. But benzoic acid, $\text{C}_7\text{H}_6\text{O}_2$, is itself composed of benzene, C_6H_6 , and carbonic anhydride, CO_2 , which also occupy equal volumes.⁸ There is an immense number of similar examples among those organic substances to whose study Gerhardt consecrated his whole life and work, and he did not allow such facts as these to escape his attention. Still more frequently in the phenomena of substitution, when two substances react on each other, and two are produced without a change of volume, it is found that the two sub-

⁷ This is not only seen from the above calculations, but may be proved by experiment. A glass tube, divided in the middle by a stopcock, is taken and one portion filled with dry hydrogen chloride (the dryness of the gases is very necessary, because ammonia and hydrogen chloride are both very soluble in water, so that a small trace of water may contain a large amount of these gases in solution) and the other with dry ammonia, under the atmospheric pressure. One orifice (for instance, of that portion which contains the ammonia) is firmly closed, and the other is immersed under mercury, and the cock is then opened. Solid sal-ammoniac is formed, but if the volume of one gas be greater than that of the other, some of the first gas will remain. By immersing the tube in the mercury in order that the internal pressure shall equal the atmospheric pressure, it may easily be shown that the volume of the remaining gas is equal to the difference between the volumes of the two portions of the tube, and that this remaining gas is part of that whose volume was the greater.

⁸ Let us demonstrate this by figures. From 122 grams of benzoic acid there are obtained (a) 78 grams of benzene, whose density referred to hydrogen is 39, hence its relative volume is 2; and (b) 44 grams of carbonic anhydride, whose density is 22, and hence the volume is 2. It is the same in other cases.

stances acting on each other, as well as each of the two resulting substances, occupy equal volumes. Thus, in general, reactions of substitution take place between volatile acids, HX , and volatile alcohols, $R(OH)$, with the formation of ethereal salts, RX , and water, $H(OH)$, and the volume of the vapour of the reacting quantities, HX , $R(OH)$, and RX , is the same as that of water $H(OH)$, whose weight, corresponding with the formula, 18, occupies 2 volumes, if 1 part by weight of hydrogen occupy 1 volume and the density of aqueous vapour referred to hydrogen is 9. Such general examples, of which there are many,⁹ show that the reaction of equal volumes forms a chemical phenomenon of frequent occurrence, indicating the necessity for acknowledging the law of Avogadro-Gerhardt.

But the question arises, What is the relation of volumes if reaction between two substances takes place in more than one proportion, according to the law of multiple proportions? A definite answer can only be given in cases which have been very thoroughly studied. Thus chlorine, in acting on marsh gas, CH_4 , forms four compounds, CH_3Cl , CH_2Cl_2 , $CHCl_3$, and CCl_4 , and it may be established by direct experiment that the substance CH_3Cl (methyl chloride) precedes the remainder, and that the latter proceed from it by the further action of chlorine. And this substance, CH_3Cl , is formed by the reaction of equal volumes of marsh gas, CH_4 , and chlorine, Cl_2 , according to the equation $CH_4 + Cl_2 = CH_3Cl + HCl$. A great number of similar cases are met with amongst organic—that is, carbon—compounds. Gerhardt was led to the discovery of his law by investigating many such reactions, and by observing that in them the reaction of equal volumes precedes all others.

But if nitrogen or hydrogen gives several compounds with oxygen, the question proposed above cannot be answered with complete clearness, because the successive formation of the different combinations cannot be so strictly defined. It may be supposed, but neither definitely affirmed nor experimentally confirmed, that nitrogen and oxygen first give nitric oxide, NO , and only subsequently the brown vapours N_2O_3 and NO_2 . Such a sequence in the combination of

⁹ A large number of such generalised reactions, showing reaction by equal volumes, occur in the case of the hydrocarbon derivatives, because many of these compounds are volatile. The reactions of alkalies on acids, or anhydrides on water, &c., which are so frequent between mineral substances, present but few such examples, because many of these substances are not volatile and their vapour densities are unknown. But essentially the same is seen in these cases also; for instance, sulphuric acid, H_2SO_4 , breaks up into the anhydride, SO_3 , and water, H_2O , which exhibit an equality of volumes. Let us take another example where three substances combine in equal volumes: carbonic anhydride, CO_2 , ammonia, NH_3 , and water, H_2O (the volumes of all are equal to 2), form acid ammonium carbonate, $(NH_4)HCO_3$.

nitrogen with oxygen can only be assumed on the basis of the fact that NO forms N_2O_3 and NO_2 directly with oxygen. If it be admitted that NO (and not N_2O or NO_2) be first formed, then this instance would also confirm the law of Avogadro-Gerhardt, because nitric oxide contains equal volumes of nitrogen and oxygen. So, also, it may be admitted that, in the combination of hydrogen with oxygen, hydrogen peroxide is first formed (equal volumes of hydrogen and oxygen), which is decomposed by the heat evolved into water and oxygen. This explains the presence of traces of hydrogen peroxide (Chapter IV.) in almost all cases of the combustion or oxidation of hydrogenous substances; for it cannot be supposed that water is first formed and then the peroxide of hydrogen, because up to now such a reaction has not been observed, whilst the formation of H_2O from H_2O_2 is very easily reproduced.¹⁰

Thus a whole series of phenomena show that the chemical reaction of substances actually takes place, as a rule, between equal volumes, but this does not preclude the possibility of the frequent reaction of unequal volumes, although, in this case, it is often possible to discover a preceding reaction between equal volumes.¹¹

The law of Avogadro-Gerhardt may also be easily expressed in an algebraical form. If the weight of a molecule, or of that quantity of a substance which enters into chemical reaction and occupies in a state of vapour, according to the law, a volume equal to that occupied by the

¹⁰ This opinion, which I have always held (since the appearance of the first editions of this work), as to the primary origin of hydrogen peroxide and of the formation of water by means of its decomposition, has in latter days become more generally accepted, thanks more especially to the work of Traube. Probably it explains most simply the necessity for the presence of traces of water in many reactions, as, for instance, in the explosion of carbonic oxide with oxygen, and perhaps the theory of the explosion of detonating gas itself and of the combustion of hydrogen will gain in clearness and truth if we take into consideration the preliminary formation of hydrogen peroxide and its subsequent decomposition.

¹¹ The possibility of reactions between unequal volumes, notwithstanding the general applicability of the law of Avogadro-Gerhardt, may, in addition to what has been said above, depend on the fact that the participating substances, at the moment of reaction, undergo a preliminary modification, decomposition, isomeric (polymeric) transformation, &c. Thus, if NO_2 seems to proceed from N_2O_4 , if O_2 is formed from O_3 , and the converse, then it cannot be denied that the production of molecules containing only one atom—for instance, of oxygen—is also possible, as also is that of higher polymeric types, e.g., the molecule N from N_2 , or H_3 from H_2 . In this manner it is obviously possible, by means of a series of hypotheses, to explain the case of the formation of ammonia, NH_3 , from 3 vols. of hydrogen and 1 vol. of nitrogen. But it must be observed that perhaps our information in similar instances is, as yet, far from being complete. If hydrazine or diamide, N_2H_4 , is formed and the imide N_2H_2 in which 2 vols. of hydrogen are combined with 2 vols. of nitrogen, then the reaction here perhaps first takes place between equal volumes. If it appears that the less stable imide, N_2H_2 , is formed before NH_3 , and splits up with the formation of ammonia, then the first reaction will proceed between equal volumes of nitrogen and hydrogen.

molecules of other bodies, be indicated by the letters M_1, M_2, \dots or, in general, M , and if the letters D_1, D_2, \dots or, in general, D , stand for the density or weight of a given volume of the gases or vapours of the corresponding substances under certain definite conditions of temperature and pressure, then the law requires that

$$\frac{M_1}{D_1} = \frac{M_2}{D_2} \dots = \frac{M}{D} = C,$$

where C is a certain constant. This expression shows directly that the volumes corresponding with the weights M_1, M_2, \dots, M , are equal to a certain constant, because the volume is proportional to the weight and inversely proportional to the density. The magnitude of C is naturally conditioned by and dependent on the units taken for the expression of the weights of the molecules and the densities. The weight of a molecule (equal to the sum of the atomic weights of the elements forming it) is usually expressed by taking the weight of an atom of oxygen as 16; then the weight of an atom of hydrogen is 1.008 (i.e., approximately 1), and hydrogen is now generally chosen as the unit for the expression of the densities of gases and vapours; it is therefore only necessary to find the magnitude of the constant for any one compound, as it will be the same for all others. Let us take water. Its reacting mass is expressed (conditionally and relatively) by the formula or molecule H_2O , for which $M = 18.016$ (or nearly 18) if $O = 16$ and $H = 1.008$, as we already know from the composition of water. Its vapour density, or D , compared with hydrogen is approximately 9, and consequently for water $C = 2$, and therefore, in general, for the molecules of all substances $\frac{M}{D} = 2$.

Consequently the weight of a molecule is equal (or rather nearly equal) to twice its vapour density expressed relatively to that of hydrogen, and conversely **the density of a gas is (nearly) equal to half the molecular weight referred to hydrogen.**

The truth of this may be seen by comparing a very large number of observed vapour densities with the results obtained by calculation. As an illustration, we may point out that for ammonia, NH_3 , the weight of the molecule or quantity of the reacting substance, as well as the composition and weight corresponding with the formula, are very nearly expressed by the figures $14 + 3 = 17$ (more exactly $14.04 + 3 \times 1.008 = 17.064$). Consequently $M = 17$. Hence, according to the law, $D = 8.5$. And this result is also obtained by experiment. The density, according to both formula and experiment, of nitrous oxide, N_2O , is 22; of nitric acid, 15; and of nitric peroxide, 23. In the case of nitrous anhydride, N_2O_3 , a substance which dissociates into $NO + NO_2$, the density should

vary between 38 (so long as the N_2O_3 remains unchanged) and 19 (when $\text{NO} + \text{NO}_2$ are obtained). There are no figures of constant density for H_2O_2 , NHO_3 , N_2O_4 , and many similar compounds which are either wholly or partially decomposed on passing into vapour. Salts and similar substances either have no vapour density because they do not pass into vapour (for instance, potassium nitrate, KNO_3) without decomposition, or, if they do pass into vapour without decomposing, their vapour density is observed only with difficulty at very high temperatures. The practical determination of the vapour density at these high temperatures (for example, for sodium chloride, ferrous chloride, stannous chloride, &c.) requires special methods which have been worked out by Sainte-Claire Deville, Crafts, Nilson and Pettersson, Meyer, Scott, and others. The difficulties of experiment having been overcome, it is found that the law of Avogadro-Gerhardt holds good for such salts as potassium iodide, beryllium chloride, aluminium chloride, ferrous chloride, &c.—that is, the density obtained by experiment proves to be equal to half the molecular weight—naturally within the limits of experimental error or of possible deviation from the law.

When the consequences of a law are verified by a great number of observations, it should be considered as confirmed by experiment. But this does not exclude the possibility of *apparent* deviations. These may evidently be of two kinds: the fraction $\frac{M}{D}$ may be found to be either greater or less than 2—that is, the calculated density may be either greater or less than the observed density. When the difference between the results of experiment and calculation falls within the possible errors of experiment (for example, when it equals only hundredths of the density), or within a possible error owing to the laws of gases having only an approximate application (as is seen from the deviations, for instance, from the law of Boyle and Mariotte), then the fraction $\frac{M}{D}$ proves to be but slightly different from 2 (between 1.9 and 2.2), and such cases as these may be classed among those which ought to be expected from the nature of the subject. It is a different matter if the quotient of $\frac{M}{D}$ be several times, and in general a multiple, *greater* or less than 2. The application of the law must then be explained or it must be laid aside, because the laws of nature admit of no exceptions. We will therefore take two such cases, and first one in which the *quotient* $\frac{M}{D}$ *is greater than 2, or the density obtained by experiment less than is in accordance with the law.*

It must be admitted, as a consequence of the law of Avogadro-Gerhardt, that there is a decomposition in those cases where the volume of the vapour corresponding with the weight of the amount of a substance entering into reaction is greater than the volume of two parts by weight of hydrogen. Suppose the density of the vapour of water to be determined at a temperature above that at which it is decomposed, then, if not all, at any rate a large proportion of the water will be decomposed into hydrogen and oxygen. The density of such a mixture of gases—detonating gas—will be less than that of aqueous vapour; it will be equal to 6 (compared with that of hydrogen), because 1 volume of oxygen weighs 16, and 2 volumes of hydrogen 2; and, consequently, 3 volumes of detonating gas weigh 18 and 1 volume 6, while the density of aqueous vapour is 9. Hence, if the density of aqueous vapour were determined after its decomposition, the quotient $\frac{M}{D}$

would be found to be 3 and not 2. This phenomenon might be considered as a deviation from Gerhardt's law, but this would not be correct, because it may be shown by means of diffusion through porous substances, as described in Chapter II., that water is decomposed at such high temperatures. In the case of water itself there can naturally be no doubt, because its vapour density agrees with the law at all temperatures at which it has been determined.¹² But there are many substances which decompose with great ease directly they are volatilised, and therefore only exist as solids or liquids, and not in a state of vapour. There are, for example, many salts of this kind, besides all definite solutions having a constant boiling-point, all the compounds of ammonia—for example, all ammonium salts—&c. Their vapour densities, determined by Bineau, Deville, and others, show that they do not agree with Gerhardt's law. Thus the vapour density of sal-ammoniac, NH_4Cl , is nearly 14 (compared with hydrogen), whilst its molecular weight is not less than 53.5, whence the vapour density should be nearly 27, according to the law. The molecule of sal-ammoniac cannot be less than NH_4Cl , because it is formed from the molecules NH_3 and HCl , and contains single atoms of nitrogen and chlorine, and therefore cannot be divided; further, it never enters into reactions with the molecules of other substances (for instance, potassium hydroxide, or nitric acid) in

¹² As the density of aqueous vapour remains constant within the limits of experimental accuracy, even at 1000° , when dissociation has certainly commenced, it would appear that only a very small amount of water is decomposed at these temperatures. If even 10 per cent. of water were decomposed, the density would be 8.57 and the quotient $M/D = 2.1$, but at the high temperatures here concerned the error of experiment is hardly less than the difference between this quantity and 2. And probably at 1000° the dissociation is far from being equal to 10 per cent. Hence the variation in the vapour density of water does not give us the means of ascertaining the starting-point of its dissociation.

quantities of less than 53·5 parts by weight, &c. The calculated density (about 27) is here double the observed density (about 13·4); hence $\frac{M}{D} = 4$ and not 2. For this reason the vapour density of sal-ammoniac for a long time served as an argument for doubting the truth of the law. But it proved otherwise, after the matter had been fully investigated. The low density depends on the decomposition of sal-ammoniac, on volatilising, into ammonia and hydrogen chloride. The observed density is not that of sal-ammoniac, but of a mixture of NH_3 and HCl , which should be nearly 14, because the density of NH_3 is 8·5, and that of HCl , 18·2, so that the density of their mixture (in equal volumes) should be about 13·4.¹³ The actual decomposition of the vapours of sal-ammoniac was demonstrated by Pebal and Than by the same method as the decomposition of water, namely, by passing the vapour through a porous substance. The experiment demonstrating the decomposition of sal-ammoniac during volatilisation may be made very easily, and is a very instructive point in the history of the Avogadro-Gerhardt law, because without its aid it would never have been imagined that sal-ammoniac decomposed in volatilising, as this decomposition shows all the signs of simple sublimation; consequently the decomposition was not proved by experiment but foretold by the law. The whole aim and practical use of the discovery of the laws of nature consists in, and is shown by, the fact that they enable the unknown to be foretold, the unobserved to be foreseen. The arrangement of the experiment is based on the following reasoning.¹⁴ According to the law and to experiment, the density of ammonia, NH_3 , is $8\frac{1}{2}$, and that of hydrochloric acid, HCl , $18\frac{1}{4}$, if the density of hydrogen is 1. Consequently, in a mixture of NH_3 and HCl , the ammonia will penetrate much more rapidly through a porous mass, or a fine orifice, than the heavier hydrochloric acid, just as in a former experiment the hydrogen penetrated more rapidly than the oxygen. Therefore, if the vapour of sal-ammoniac comes into contact with a porous mass, the ammonia will pass through it in greater quantities than the hydrochloric acid, and this excess of ammonia may be detected by means of moist red litmus paper, which should be turned

¹³ This explanation of the vapour densities of sal-ammoniac, sulphuric acid, and similar substances which decompose on being distilled was the most natural to resort to as soon as the application of the law of Avogadro-Gerhardt to chemical relations was instituted; it was, for instance, given in my work on *Specific Volumes*, 1856, p. 99. The formula, $M/D = 2$, which was applied later by many other investigators, had already been made use of in that work.

¹⁴ The beginner must remember that an experiment and the mode in which it is carried out must be determined by the principle or fact which it is intended to illustrate, and not *vice versa*, as some suppose. The idea which determines the necessity of an experiment is the chief consideration.

blue. If the vapour of sal-ammoniac were not decomposed, it would pass through the porous mass as a whole, and the colour of the litmus paper would not be altered, because sal-ammoniac is a neutral salt. Thus, by testing with litmus the substances passing through the porous mass, it may be decided whether the sal-ammoniac is decomposed or not when passing into vapour. Sal-ammoniac volatilises at so moderate a temperature that the experiment may be conducted in a glass tube heated by means of a lamp, an asbestos plug being placed near the centre of the tube.¹⁵ The asbestos forms a porous mass, which is unaltered at a high temperature. A piece of dry sal-ammoniac is placed at one side of the asbestos plug, and is heated by a Bunsen burner. The vapours formed are driven by a current of air forced from a gasometer or bag through two tubes containing pieces of moist litmus paper, one blue and one red paper in each. If the sal-ammoniac be heated, then the ammonia appears on the opposite side of the asbestos plug, and the litmus there turns blue, and as an excess of hydrochloric acid remains on the side where the sal-ammoniac is heated, it turns the litmus at that end red. This proves that sal-ammoniac, when converted into vapour, splits up into ammonia and hydrochloric acid, and at the same time gives an instance of the possibility of correctly conjecturing a fact on the basis of the Avogadro-Gerhardt law.^{15a}

So also the fact of a decomposition occurring may be proved in the other instances where $\frac{M}{D}$ proves to be greater than 2, and hence the apparent deviations are, in reality, an excellent proof of the general application and significance of the law of Avogadro-Gerhardt.

In those cases where the *quotient* $\frac{M}{D}$ proves to be *less* than 2, or the observed density *greater* than that calculated, by an integral number of times, the matter is evidently more simple, and the fact observed only indicates that the weight of the molecule is as many times greater than that taken, as the quotient obtained is less than 2. So, for instance,

¹⁵ It is important that the tubes, asbestos, and sal-ammoniac should be dry, as otherwise the moisture retains the ammonia and hydrogen chloride.

^{15a} Baker (1894) showed that the complete decomposition of NH_4Cl in the act of volatilising only takes place in the presence of water, traces of which are quite sufficient, but that in the total absence of moisture (by carefully drying with P_2O_5) there is either no decomposition, and the vapour density of the sal-ammoniac is found to be normal, i.e., nearly 27, or else only a portion of the salt is decomposed (Hartmann). It is not yet quite clear what part the trace of moisture plays here, and it must be presumed that the phenomenon belongs to the category of contact phenomena, which have not yet been fully explained (see Chap. IX., note 29). V. Kurbatoff showed that hydrochloride of aniline (which is essentially an analogue of sal-ammoniac) gives a vapour density 32.6, corresponding very nearly with its decomposition into $\text{NC}_6\text{H}_7 + \text{HCl}$, if the temperature be sufficiently high, but at lower temperatures the decomposition is not complete.

in the case of ethylene, whose composition is expressed by CH_2 , the density was found by experiment to be 14, and in the case of amylene, whose composition is also CH_2 , the density proved to be 35, and consequently the quotient for ethylene = 1, and for amylene = $\frac{2}{5}$. If the molecular weight of ethylene be taken, not as 14, as might be imagined from its composition, but as twice as great—namely, as 28—and that of amylene as five times greater—that is, as 70—then the molecular composition of the first will be C_2H_4 , and that of the second C_5H_{10} , and for both of them $\frac{M}{D}$ will be equal to 2. This application of the

law, which at first sight may appear perfectly arbitrary, is nevertheless strictly correct, because the amount of ethylene which reacts—for example, with sulphuric and other acids—is not equal to 14, but to 28 parts by weight. Thus with H_2SO_4 , Br_2 , or HI , &c., ethylene combines in a quantity C_2H_4 , and amylene in a quantity C_5H_{10} , and not CH_2 . On the other hand, ethylene is a gas which liquefies with difficulty (absolute boiling-point, $+10^\circ$), whilst amylene is a liquid boiling at 35° (absolute boiling-point, $+192^\circ$), and by admitting the greater density of the molecules of amylene ($M = 70$) its difference from the lighter molecules of ethylene ($M = 28$) becomes clear. Thus, the smaller quotient $\frac{M}{D}$ is *an indication of polymerisation*, just as the larger quotient shows decomposition. The difference between the densities of oxygen and ozone is a case in point.

On turning to the elements, it is found that, in certain cases, especially with metals—for instance, mercury, zinc, and cadmium—those weights of the atoms which must be acknowledged in their compounds (of which mention will be afterwards made) appear to be also the molecular weights. Thus the atomic weight of mercury must be taken as = 200, but the vapour density = 100, and the quotient = 2. Consequently the *molecule of mercury contains one atom*, Hg. It is the same with sodium, cadmium, and zinc. This is the simplest molecule, which necessarily is only possible **in the case of elements**, as the molecule of a compound must contain at least two atoms. However, the molecules of many of the elements prove to be complex—for instance, the weight of an atom of oxygen is 16, and its density is also 16, so that its molecule must contain two atoms, O_2 , which might already be concluded by comparing its density with that of ozone, whose molecule contains O_3 (Chapter IV.). So also the molecules of hydrogen, H_2 , of chlorine, Cl_2 , of nitrogen, N_2 , &c., all contain 2 atoms. If chlorine reacts with hydrogen, the volume remains unaltered after the formation of hydrochloric acid, $\text{H}_2 + \text{Cl}_2 = 2\text{HCl}$. It is a case of substitution

between the one and the other, and therefore the volumes remain constant. There are elements whose molecules are much more complex—for instance, sulphur, S_6 —although, by heating, the density is reduced to a third, and S_2 is formed. Judging from the vapour density of phosphorus ($D = 62$), the molecule contains four atoms, P_4 . Hence many elements when polymerised appear in molecules which are more complex than the simplest possible. In carbon, as we shall afterwards find, a very complex molecule must be admitted, as otherwise its non-volatility and other properties cannot be understood. And if compounds are decomposed by a more or less powerful heat, and if polymeric substances are *de-polymerised* (that is, the weight of the molecule diminishes) by a rise of temperature, as N_2O_4 passes into NO_2 , or ozone, O_3 , into ordinary oxygen, O_2 , then we *might expect to find the splitting-up of the complex molecules of elements* into the simplest molecule containing a single atom only—that is to say, if O_2 be obtained from O_3 , then the formation of O might also be looked for. The possibility, but not the proof, of such a proposition is indicated by the *vapour of iodine*. Its normal density is 127 (Dumas, Deville, and others), which corresponds with the molecule I_2 . At temperatures above 800° (up to which the density remains almost constant), this density distinctly decreases, as is seen from the verified results obtained by Victor Meyer, Crafts, and Troost. At the ordinary pressure and a temperature of 1000° it is about 100, at 1250° about 80, at 1400° about 75, and it apparently strives to reduce itself to one-half—that is, to 63. Under a reduced pressure this splitting-up, or de-polymerisation, of iodine vapour actually goes on until a density¹⁶ of 66 is reached, as Crafts demonstrated by reducing the pressure to 100 mm. and raising the temperature to 1500° . From this it may be concluded that at high temperatures and low pressures the molecule I_2 gradually passes into the molecule I containing one atom like that of mercury, and that something similar occurs with other elements with a considerable rise of temperature, which tends to bring about the disunion of compounds and the decomposition of complex molecules.¹⁷

¹⁶ Just as we saw (Chap. VI., note 46) an increase in the dissociation of N_2O_4 and the formation of a large proportion of NO_2 , with a decrease of pressure. The decomposition of I_2 into $I + I$ is a similar dissociation.

¹⁷ Although at first a similar phenomenon was recognised in the case of chlorine, it was afterwards proved that if there is a decrease of density it is only a small one. In the case of bromine it is not much greater, and is far from being equal to that for iodine.

As in general we very often involuntarily confuse chemical with physical processes, it may be that a physical process of change in the coefficient of expansion with a change of temperature acts together with a change in molecular weight, and partially, if not wholly, accounts for the decrease of the densities of chlorine, bromine, and iodine. Thus I have remarked (*Comptes Rendus*, 1876) that the coefficient of expansion of gases increases with

Besides these two cases of **apparent** discrepancy from the law of Avogadro-Gerhardt there is yet a third, which is the last, and is very instructive. In the investigation of separate substances they have to be isolated in the purest possible form, and their chemical and physical properties, and among them the vapour density, then determined. If the latter be normal—that is, if $D = M/2$ —it often serves as a proof of the purity of the substance, i.e., of its freedom from all foreign matter. If it be abnormal—that is, if D be not equal to $M/2$ —then for those who do not believe in the law it appears as a new argument against it; but to those who have already grasped the important significance of the law it becomes clear that there is some error in the observation, or that the density was determined under conditions in which the vapour does not follow the laws of Boyle and Gay-Lussac, or else that the substance has not been sufficiently purified, and contains other substances. In that case the law of Avogadro-Gerhardt furnishes convincing evidence of the necessity of a fresh and more exact research. And as yet the causes of error have always been found. There are not a few examples in point in the recent history of chemistry. We will cite one instance. In the case of pyrosulphuryl chloride, $S_2O_5Cl_2$, $M = 215$,^{17a} and consequently D should be 107.5, instead of which Ogier and others obtained 53.8—that is, a density half as great—and, further, Ogier (1882) demonstrated clearly that the substance is not dissociated by distillation into SO_3 and SO_2Cl_2 , or any other two products, and thus the abnormal density of $S_2O_5Cl_2$ remained unexplained until D. P. Konovaloff (1885) showed that the previous investigators were working with a mixture (containing SO_3HCl), and that pyrosulphuryl chloride has a normal density of approximately 107. Had not the law of Avogadro-Gerhardt served as a guide, the impure liquid would have still passed as pure; the more so since the determination of the amount of chlorine could not aid in the discovery of the impurity. Thus, by following a true law of nature we are led to true deductions.

All cases which have been studied confirm the law of Avogadro-

their molecular weight, and (Chap. II., note 26) the results of direct experiment show the coefficient of expansion of hydrobromic acid ($M = 81$) to be 0.00386 instead of 0.00367, which is that of hydrogen ($M = 2$). Hence, in the case of the vapour of iodine ($M = 254$) a very large coefficient of expansion is to be expected, and from this cause alone the relative density would fall. Taking the coefficient of expansion of iodine vapour as 0.004, at 1000° its density would be 116. So that the dissociation of iodine may be only an apparent phenomenon. However, on the other hand, the heavy vapour of mercury ($M = 200$, $D = 100$) scarcely decreases in density at a temperature of 1500° ($D = 98$, according to Victor Meyer); but it must not be forgotten that the molecule of mercury contains only one atom, whilst that of iodine contains two, and this is very important.

^{17a} For the sake of simplicity and clearness the atomic weights are given here in round numbers; for instance, $H = 1$, $O = 16$, $C = 12$, $S = 32$, $N = 14$, $Cl = 35.5$, &c.

Gerhardt, and as by it a deduction is obtained, from the determination of the vapour density (a purely physical property), as to the weight of the molecule or quantity of a substance entering into chemical reaction, this law links together the two branches of knowledge—physics and chemistry—in the most intimate manner. Besides which the law of Avogadro-Gerhardt places the conceptions of **molecules** and **atoms** on a firm foundation, which was previously wanting. Although since the days of Dalton it had become evident that it was necessary to admit the existence of the elementary atom (the chemical individual indivisible by chemical or other forces), and of the groups of atoms (or molecules) of compounds, indivisible by mechanical and physical forces, still the relative magnitude of the molecule and atom was not defined with sufficient clearness. Thus, for instance, the atomic weight of oxygen might be taken as 8 or 16, or any multiple of these numbers, and nothing indicated a reason for the acceptance of one rather than another of these magnitudes;¹⁸ while as regards the weights of the molecules of elements and compounds there was no trustworthy knowledge whatever. With the establishment of Gerhardt's law the idea of the molecule was fully defined, as well as the relative magnitude of the elementary atom.

The chemical particle or **molecule must be considered as the quantity of a substance which enters into chemical reaction with other molecules, and occupies in a state of vapour the same volume as two parts by weight of hydrogen.**

The molecular weight (which has been indicated by *M*) of a substance is determined by its composition, transformations, and vapour density.

The molecule is not divisible by the mechanical and physical changes of substances, but in chemical reactions it is altered either in

¹⁸ And so it was in the fifties. Some took $O=8$, others $O=16$, H being 1. Water in the first case would be HO and hydrogen peroxide HO_2 , and in the second case, as is now generally accepted, water H_2O , and hydrogen peroxide H_2O_2 or HO . Disagreement and confusion reigned. In 1860 the chemists of the whole world met at Carlsruhe for the purpose of arriving at some agreement and uniformity of opinion. I was present at this Congress, and well remember how great was the difference of opinion, and how a compromise was advocated with great acumen by many scientific men, and with what warmth the followers of Gerhardt, at whose head stood the Italian professor Canizzaro, followed up the consequences of the law of Avogadro. In the spirit of scientific freedom, without which science would make no progress, and would remain petrified as in the middle ages, and with the simultaneous necessity of scientific conservatism, without which the roots of past study could give no fruit, a compromise was not arrived at, nor ought it to have been, but instead of it truth, in the form of the law of Avogadro-Gerhardt, received by means of the Congress a wider development, and soon afterwards convinced all minds. Then the new so-called *Gerhardt* atomic weights established themselves, and in the seventies they were already in general use.

its properties, or quantity, or structure, or in the nature of the motion of its parts.

An agglomeration of molecules, which are alike in all chemical respects, makes up the masses of homogeneous substances in all states.¹⁹

Molecules consist of atoms in a certain state of distribution and motion, just as the solar system²⁰ is made up of inseparable parts (the sun, planets, satellites, comets, &c.). The greater the number of atoms in a molecule, the more complex is the resultant substance. The equilibrium between the dissimilar atoms may be more or less stable, and may for this reason give more or less stable substances. Physical and mechanical transformations alter the velocity of the motion of, and the distances between, either the individual molecules, or the atoms in the molecules, or of their sum total, but they do not alter the original equilibrium of the system; whilst chemical changes, on the other hand, alter the molecules themselves, that is, the velocity of motion, the relative distribution, and the quality and quantity of the atoms in the molecules.

Atoms are the smallest quantities or chemically indivisible masses **of the elements forming the molecules** of elements and compounds.

Atoms have weight, the sum of their weights forms the weight of the molecule, and the sum of the weights of the molecules forms the weight of masses, and is the cause of gravity, and of all the phenomena which depend on the mass of a substance.

The elements are characterised, not only by their independent exist-

¹⁹ If the aggregation of all kinds of heterogeneous molecules be possible in a gaseous state, where the molecules are considerably removed from each other, then in a liquid state, where they are already close together, such an aggregation becomes possible only in the sense of the mutual reaction which results from their chemical attraction for each other, and especially the aptitude of heterogeneous molecules for combining together. Solutions and other so-called indefinite chemical compounds should be regarded in this light. According to the principles developed in this work we should regard them as containing both the compounds of the heterogeneous molecules themselves and the products of their decomposition, as in peroxide of nitrogen, N_2O_4 and NO_2 .

²⁰ This strengthens the fundamental idea of the unity and harmony of type of all creation, and is one of those ideas which impress themselves on man in all ages, and give rise to a hope of arriving in time, by means of a laborious series of discoveries, observations, experiments, laws, hypotheses, and theories, at a comprehension of the internal and invisible structure of concrete substances with that same degree of clearness and exactitude which has been attained in the visible structure of the heavenly bodies. It is not many years ago since the law of Avogadro-Gerhardt took root in science. It is within the memory of many living scientific men, and of mine amongst others. It is not surprising, therefore, that as yet little progress has been made in the province of molecular mechanics; but the theory of gases alone, which is intimately connected with the conception of molecules, shows by its success that the time is approaching when our knowledge of the internal structure of matter will be defined and established.

ence, their incapacity of being converted into each other, &c., but also by the weights of their atoms.

The chemical and physical properties of a substance depend on the weight, composition, and properties of the molecules forming it, and on the weight, properties, and distribution (structure, motion) of the atoms forming the molecules.

This is the substance of those principles of **molecular mechanics** which lie at the basis of all contemporary physical and chemical constructions since the establishment of the law of Avogadro-Gerhardt. The fecundity of the principles enunciated is seen at every step in all the particular cases forming the present store of chemical data. We will here cite a few examples of the application of the law.

As the weight of an atom must be understood as the minimum quantity of an element entering into the composition of all the molecules formed by it, we may, in order to find the weight of an atom of oxygen, take the molecules of those of its compounds which have already been described, together with the molecules of certain of those carbon compounds which will be described in the following chapter:—

	Molecular Weight	Amount of Oxygen		Molecular Weight	Amount of Oxygen
H ₂ O	18	16	HNO ₃	63	48
N ₂ O	44	16	CO	28	16
NO	30	16	CO ₂	44	32
NO ₂	46	32			

The number of substances taken might be considerably increased, but the result would be the same—that is, the molecules of the compounds of oxygen would never be found to contain less than 16 parts by weight of this element, but always $n16$, where n is a whole number. The molecular weights of the above compounds are found either directly from the densities of their vapours or gases, or from their reactions. Thus the vapour density of nitric acid (as a substance which easily decomposes above its boiling-point) cannot be accurately determined, but the fact of its containing one part by weight of hydrogen, as also all its properties and reactions, indicate the above molecular composition and no other. In this manner it is very easy to find the atomic weight of all the elements, knowing the molecular weights and compositions of their compounds. It may, for instance, be easily proved that less than $n12$ parts of carbon never enters into the molecules of carbon compounds, and therefore C must be taken as 12, and not as 6, which was the number in use before Gerhardt. In a similar manner the atomic weights now

accepted for the elements oxygen, nitrogen, carbon, chlorine, sulphur, &c., were found and indubitably established, and they are even now termed the Gerhardt atomic weights. As regards the metals, many of which do not give a single volatile compound, we shall afterwards see that there are also methods by which their atomic weights may be established, but nevertheless the law of Avogadro-Gerhardt is here also ultimately resorted to in order to remove any doubt which may be encountered. Thus, for instance, although much that was known concerning the compounds of beryllium necessitated its atomic weight being taken as $\text{Be}=9$ —that is, the oxide as BeO and the chloride as BeCl_2 —still certain analogies gave reason for considering its atomic weight to be $\text{Be}=13\cdot5$, in which case its oxide would be expressed by the composition Be_2O_3 , and the chloride by BeCl_3 .²¹ It was then found that the vapour density of beryllium chloride was approximately 40, when it became quite clear that its molecular weight was 80; and as this satisfies the formula BeCl_2 , but does not suit the formula BeCl_3 , it became necessary to regard the atomic weight of Be as 9 and not as $13\frac{1}{2}$.

With the establishment of a true conception of molecules and atoms, chemical formulæ became direct expressions, not only of composition,²² but also of molecular weight or **vapour density**, and conse-

²¹ If $\text{Be}=9$, and beryllium chloride be BeCl_2 , then for every 9 parts of beryllium there are 71 parts of chlorine, and the molecular weight of $\text{BeCl}_2=80$; hence the vapour density should be 40 or $n40$. If $\text{Be}=13\cdot5$, and beryllium chloride be BeCl_3 , then to 13·5 of beryllium there are 106·5 of chlorine; hence the molecular weight would be 120, and the vapour density 60 or $n60$. The composition is evidently the same in both cases, because $9 : 71 :: 13\cdot5 : 106\cdot5$. Thus, if the symbol of an element designate different atomic weights, apparently very different formulæ may equally well express both the percentage composition of compounds and those properties which are required by the laws of multiple proportions and equivalents. The choice of one or the other multiple quantity for the atomic weight is impossible without a firm and concrete conception of the molecule and atom, and this is only obtained as a consequence of the law of Avogadro-Gerhardt, and hence the modern atomic weights are the results of this law.

²² In general, when it is required to transfer a formula into its percentage composition, we must replace the symbols by their corresponding atomic weights and find their sum, and knowing the amount by weight of a given element in it, it is easy by proportion to find the amount of this element in 100 or any other number of parts by weight. If, on the contrary, it be required to find the formula from a given percentage composition, we must proceed as follows: Divide the percentage amount of each element entering into the composition of a substance by its atomic weight and compare the figures thus obtained—they should be in simple multiple proportion to each other. Thus, for instance, from the percentage composition of hydrogen peroxide, 5·88 of hydrogen and 94·12 of oxygen, it is easy to find its formula; it is only necessary to divide the amount of hydrogen by unity and the amount of oxygen by 16. The numbers 5·88 and 5·88, which are thus obtained, are in the ratio 1 : 1, which means that in hydrogen peroxide there is one atom of hydrogen to one atom of oxygen.

It may be further observed that even the very language or nomenclature of chemistry acquires a particular clearness and conciseness by means of the conception of molecules, because then the names of substances may directly indicate their composition. Thus

quently of a series of fundamental chemical and physical data, inasmuch as a number of the properties of substances are dependent on their vapour density, or molecular weight and composition. The vapour density $D = \frac{M}{2}$. For instance, the formula of ethyl ether is $C_4H_{10}O$,

corresponding with the molecular weight 74, and the vapour density 37, which is the number actually found. Therefore the density of vapours and gases has ceased to be an empirical magnitude obtained by experiment only, and has acquired a rational meaning. It is only necessary to remember that 2 grams of hydrogen, or the molecular weight of this primary gas in grams, occupies at 0° and 760 mm. pressure a volume of 22.3 litres (or 22,300 cubic centimetres) in order to directly determine the weights of cubical measures of gases and vapours from their formulæ, because **the molecular weights in grams of all other vapours at 0° and 760 mm. occupy the same volume, 22.3 litres.** Thus, for example, in the case of carbonic anhydride, CO_2 , the molecular weight $M=44$; hence 44 grams of carbonic anhydride at 0° and 760 mm. occupy a volume of 22.3 litres—consequently a litre weighs 1.97 gram. By combining the laws of gases—Gay-Lussac's, Mariotte's, and Avogadro-Gerhardt's—we obtain²³ a general formula for gases:

$$6200s(273+t) = Mp,$$

where s is the weight in grams of a cubic centimetre of a vapour or gas at a temperature t and pressure p (expressed in centimetres of mercury) if the molecular weight of the gas $=M$ (expressed on the basis that the atomic weight of O is 16, and that of H, 1.008). Thus, for instance, at 100° and 760 millimetres pressure (i.e., at the atmospheric pressure)

the term 'carbon dioxide' tells more about and expresses CO_2 better than carbonic acid gas, or even carbonic anhydride. Such nomenclature is already employed by many. But expressing the composition without an indication or even hint as to the properties would be neglecting the advantageous side of the present nomenclature. Sulphur dioxide, SO_2 , expresses the same as barium dioxide, BaO_2 , but sulphurous anhydride indicates the acid properties of SO_2 . Probably in time one harmonious chemical language will succeed in embracing both advantages.

²³ This formula (which is given in my work on *The Pressure of Gases* and in a somewhat modified form in the *Comptes Rendus*, February 1876) is deduced in the following manner. According to the law of Avogadro-Gerhardt, $M=2D$ for all gases, where M is the molecular weight and D the density referred to that of hydrogen. But it is equal to the weight s_0 of a cubic centimetre of a gas in grams (at 0° and 76 cm. pressure) divided by 0.00008994, for this is the weight in grams of a cubic centimetre of hydrogen. But the weight s of a cubic centimetre of a gas at a temperature t and under a pressure p (in centimetres) is equal to $s_0p/76(1+at)$. Therefore $s_0=s.76(1+at)p$; hence $D = 76.s(1+at)/0.0000898p$, so that $M=152s(1+at)/0.00008994p$, which gives the above expression, for $1/a=273$, and 152 multiplied by 273 and divided by 0.00008994 is nearly 6200. In place of s , m/v may be taken, where m is the weight and v the volume of a vapour.

molecules. Q.E.D.²⁶ The specific heats of gases (Chapter XIV.), and many of their other properties are determined by their density, and consequently by their molecular weight. Gases and vapours in passing into a liquid state evolve the so-called **latent heat** (i.e., a portion of the internal energy of the motion of the molecules is converted into heat energy), which also proves to have a connection with the molecular weight. The observed latent heats of evaporation of carbon bisulphide, CS_2 , 86 ; of ether, $\text{C}_4\text{H}_{10}\text{O}$, 84 ; of benzene, C_6H_6 , 94 ; of alcohol, $\text{C}_2\text{H}_6\text{O}$, 201 ; of chloroform, CHCl_3 , 55, &c., show the amounts of heat expended in converting one part by weight of the above substances into vapour. A great uniformity is observed if the measure of this heat be referred to the weight of the molecule. For carbon bisulphide, the formula CS_2 expresses a weight 76 ; hence the latent heat of evaporation referred to the molecular quantity $\text{CS}_2 = 76 \times 86 = 6,536$, for ether = 6,216, for benzene = 7,332, for alcohol = 9,246, for chloroform = 6,902, for water = 9,640, &c. That is, for molecular quantities, the latent heat varies comparatively little, only from 6,000 to 10,000 heat units, whilst for equal parts by weight it is ten times greater for water than for chloroform and many other substances.²⁷

²⁶ The velocity of the transmission of sound through gases and vapours bears closely on this. It has the value $\sqrt{Kpg/D (1 + \alpha t)}$, where K is the ratio between the two specific heats (it is approximately 1.4 for gases containing two atoms in a molecule), p the pressure of the gas expressed by weight (that is, the pressure expressed by the height of a column of mercury multiplied by the density of mercury), g the acceleration of gravity, D the weight of a cubic measure of the gas, $\alpha = 0.00367$, and t the temperature. Hence, if K be known, as well as D , which can be found from the composition of a gas, we can calculate the velocity of the transmission of sound in that gas. Or if this velocity be known, we can find K . The relative velocities of sound in two gases can be easily determined (Kundt).

If a horizontal glass tube (about 1 metre long and closed at both ends) full of any gas, be firmly fixed at its middle point, it is easy to bring the tube and gas into a state of vibration by rubbing it from centre to end with a damp cloth. The vibration of the gas is easily rendered visible if the interior of the tube be dusted with lycopodium (the yellow powder-dust or spores of the lycopodium plant, which is often employed in medicine) before the gas is introduced and the tube fused up. The fine lycopodium powder arranges itself in patches, whose number depends on the velocity of sound in the gas. If there be 10 patches, then the velocity of sound in the gas is ten times slower than in glass. It is evident that this is an easy method of comparing the velocity of sound in gases. It has been demonstrated by experiment that the velocity of sound in oxygen is four times less than in hydrogen, and the square roots of the densities and molecular weights of hydrogen and oxygen stand also in this ratio.

²⁷ If the conception of the molecular weights of substances does not directly give an exact law when applied to the latent heat of evaporation, at all events it brings to light a certain uniformity in figures, which otherwise only represent the simple result of observation. Molecular quantities of liquids appear to require almost equal amounts of heat for their evaporation. The laws of thermodynamics show a more intimate connection between the latent heat of evaporation L and the molecular weight M , in dependence on the absolute boiling-point $T = 273 + t$ (Personne, Ramsay, de Forcrand, Le Chatelier, Konvaloff, &c.), which is also seen in the empirical **law of Trouton**, $\frac{L \cdot M}{T} = \text{a constant}$, which

Generalising from the above, the weight of the molecule determines the properties of a substance *independently of its composition*—i.e., of the number and quality of the atoms entering into the molecule—whenever the substance is in a gaseous state (for instance, the density of gases and vapours, the velocity of sound in them, their specific heat, &c.), or passes into that state, as we see in the latent heat of evaporation. This is intelligible from the point of view of the atomic theory in its present form, for, besides a rapid motion proper to the molecules of gaseous bodies, it is further necessary to postulate that these molecules are dispersed in space (filled throughout with the so-called luminiferous ether) like the heavenly bodies distributed throughout the universe. Here, as there, it is only the degree of removal (the distance) and the masses of substances which take effect, whilst those peculiarities of a substance which are expressed in chemical transformations, and only come into action on near approach or on contact, are in abeyance by reason of the dispersal. Hence it is at once obvious, in the first place, that in the case of solids and liquids, in which the molecules are closer together than in gases and vapours, a greater complexity is to be expected, i.e., a dependence of all the properties not only upon the weight of the molecule but also upon its composition and quality, or upon the properties of the individual chemical atoms forming the molecule; and, in the second place, that, in the case of a small number of molecules of any substance being disseminated through a mass of another substance—for example, in the formation of weak (dilute) solutions (although in this case there is an act of chemical reaction—i.e., a combination, decomposition, or substitution)—the dispersed molecules will alter the properties of the medium in which they are dissolved, almost in proportion to the molecular weight and almost independently of their composition. The greater the number of molecules—i.e., the stronger the solution—the more clearly defined will become those properties which depend upon the

varies, according to the results of experiment (when there is no decomposition), from $C = 19$ to $C = 26$, but is most often nearly 21, as is seen from the following examples:—

	t	L	M	C
Bromine, Br_2 . . .	61·6°	43·7	160	20·9
Mercury, Hg . . .	357°	62	200	19·7
CS_2	46·6°	85·7	76	20·4
C_6H_6	80·2°	93·6	78	20·6
$\text{C}_6\text{H}_7\text{N}$	184·5°	104·7	93	21·2

For water and alcohol C is about 25·9, but, judging by their capillarity, these exhibit, as Ramsay and others observed, a certain discrepancy which is considered more fully in physical chemistry. I would only remark that these discrepancies do not obscure the general application of Trouton's law, and therefore if L and t be known, it is possible to *approximately* determine M , just as in the case of the depression of solutions, as will be presently explained (see note 27a).

composition of the dissolved substance and its relation to the molecules of the solvent, for the distribution of one kind of molecules in the sphere of attraction of others cannot but be influenced by their mutual chemical reaction. These general considerations give a starting-point for explaining why, since the appearance of van't Hoff's memoir (1886), 'The Laws of Chemical Equilibrium in a Diffused Gaseous or Liquid State' (see Chapter I., note 19), it has been found more and more that *dilute* (weak) solutions exhibit such variations of properties as depend wholly upon the weight and number of the molecules and not upon their composition, and even give the means of determining the weight of molecules by studying the variations of the properties of a solvent on the introduction of a small quantity of a substance passing into solution. Although this subject has been already partially considered in the first chapter (in speaking of solutions), we touch upon it here because the meaning and importance of molecular weights are seen in it in a new and peculiar light, and because it gives a method for determining them in the event of a substance being non-volatile but capable of forming solutions. Details upon this new and complicated subject must, however, be sought in works on physical chemistry. Of the numerous properties of dilute solutions which have been investigated (for instance, the osmotic pressure, depressions, vapour pressure, boiling-point, internal friction, capillarity, variation with change of temperature, specific heat, electro-conductivity, index of refraction, &c.), we will cursorily consider the osmotic pressure and the 'depression' or fall of the temperature of freezing (Raoult's cryoscopic method), not only because these methods have been the most studied, but also because the latter is the most easily carried out and most frequently applied for determining the weight of the molecules of substances in solution, although, owing to the novelty of the subject, there are here also many experimental anomalies which cannot as yet be explained by theory.

Osmotic Pressure.—It is found by direct experiment that when a solution, held in a membrane which transmits the solvent but not the substance dissolved (dialysis), is placed in a vessel containing the solvent only, it draws in a certain amount of the solvent, and by so doing raises the pressure within the membrane until it attains a limit called the 'osmotic pressure' of the solution. This happens, for instance, when a porous vessel containing a solution of sugar in water (in whose pores a gelatinous precipitate has been deposited by the action of ferricyanide of potassium on a solution of a copper salt) is immersed in water. The rise of pressure within the membrane may be noted and expressed in terms of the column of mercury supported, and therefore in fractions of the atmospheric pressure by taking one atmosphere as equal to

76 cm. of mercury. With strong solutions the rise of pressure is considerable, and always varies with the strength of the solution. With dilute solutions the pressure is found to be almost proportional to the strength of the solution. This proves that the pressure is produced by the substance dissolved. Thus the osmotic pressure of a solution of 1 part by weight of sugar in 100 parts of water is $\frac{2}{3}$ atmosphere (at the ordinary temperature), while that of a 2 per cent. solution is $1\frac{1}{2}$ atmosphere. Hence there is no difficulty in measuring the value of the osmotic pressure with accuracy, and experiment proves that it varies with the temperature in just the same manner as the vapour pressure of a confined gas. This fact suffices to show that there is a perfect parallelism between the dissolution or dispersion of a substance in passing into a dilute solution and in passing into a state of vapour or gas. A series of observations made by Pfeffer, Traube, Devries, Naccari, Ladenburg, Tammann, and others, and generalised by van't Hoff, showed that the osmotic pressure is also dependent upon the molecular weight and volume of the substance in solution, just as is the case in the gaseous state. Therefore the osmotic pressure p or h may be calculated in dependence upon the molecular weight M , or conversely, by the above formula for the gaseous or vaporous state of matter. As an example we will take a 1 per cent. solution of sugar, $C_{12}H_{22}O_{11}$, for which $M=342\cdot18$. In this case the weight $m=1$ gram, and v , or the volume, is determined by the sp. gr., and is nearly 100·5 c.c. Therefore, according to the last of the above formulæ (II),

$$342\cdot18 = \frac{81\cdot6 \times 1 \times (273 + t)}{100\cdot5h}$$

whence the osmotic pressure h in atmospheres is

$$h = 0\cdot002373 (273 + t).$$

Pfeffer (1877, nine years before van't Hoff made his generalisation) observed the osmotic pressure of such a 1 per cent. solution of sugar at different temperatures, and his results are given in the accompanying table, together with those given by calculation according to the above formula :—

1 per cent. Solution of Sugar.	Osmotic Pressures.	
	According to Pfeffer.	According to Theory.
$t = 7^{\circ}$	0·664 atmosphere	0·664 atmosphere
14°	0·681 „	0·681 „
22°	0·721 „	0·700 „
32°	0·716 „	0·724 „
36°	0·746 „	0·733 „

It is hence evident that the results of calculation entirely (naturally

within the limits of possible error of experiment) agree with those of experiment, and therefore *the molecular weight of a substance* (which is not saline, not an electrolyte) *may be determined from the osmotic pressure of its dilute solutions*. Thus, if M be calculated by the formula from the average of Pfeffer's observations, it is found to be nearly 342, which is very nearly the value of the molecular weight of sugar according to its formula, $C_{12}H_{22}O_{11}$, and its reactions.

Beyond the fact that the solutions of saline substances (electrolytes) give disturbing anomalies (the observed pressure being greater than that obtained by calculation, and the molecular weight obtained less than the actual weight, Chap. I., note 49) in the above rule, which are, however, met with in all other methods of determining the molecular weight of substances in solution, the osmotic method of determining the molecular weight M presents some inconvenience in its practical experimental aspect, as it is difficult to prepare closed vessels whose walls will transmit the various solvents, and not permit the passage of the substance dissolved; and as such walls are incapable of sustaining high pressures (this may be overcome by employing isotonic solutions giving equal osmotic pressures), this method, although of great theoretical importance, is generally replaced in practice by other more convenient ones. These methods are all essentially based on the fact that all those cases where the solvent or substance dissolved separates out from a solution exhibit the same simplicity of relations as the osmotic pressure. And isotonic solutions (i.e., those having equal osmotic pressures) have all the same vapour pressure (i.e., an equal fall of boiling-point) and one and the same depression (i.e., equal fall of the temperature of separation of the solvent in a solid form), &c., which gives the possibility of determining the molecular weight by those properties of solutions just as well as by the osmotic pressure. Among these the **cryoscopic** or **depression** method is the one most usually resorted to, not only because it was worked out more fully and earlier than the others by Rudorff, de Coppet, Raoult (1882), Paterno, Ponsot, Abegg, Eijkman, Pickering, Chrushchoff, and others, but also because the great variety of solvents which are able to pass into the solid and liquid states permits of its being applied to the most diverse substances, starting with metals dissolving in each other (Hg, Sn, &c.) and gases soluble in water and ending with non-volatile and oily substances soluble in corresponding liquid solvents which readily solidify, such as benzene, phenol, acetic acid, &c. The method depends essentially upon the fact that dilute solutions (of non-electrolytes) follow the formula:

$$\frac{\Delta}{q} \cdot M = C = \frac{0.02(273 + t)^2}{w}.$$

where Δ is the depression (difference between the melting-points of the pure solvent and of the solution taken), q the amount by weight of the substance dissolved per 100 parts by weight of the solvent, and M the molecular weight of the substance dissolved. The first portion of the equation is called the 'molecular depression.' For a given dilute solution the molecular depression (of non-electrolytes) tends to reach a constant value, C , as the dilution increases, and this constant is determined, as the equation shows, by two factors of the solvent, namely, t , its melting-point, and w , its latent heat of fusion. In the case of water $t=0$ and $w=79$, and therefore with dilute aqueous solutions :

$$C = \frac{0.02 \times 273^2}{79} = \frac{\Delta}{q} M = 18.9,$$

or

$$\Delta = \frac{18.9q}{M}.$$

Hence with aqueous solutions $M = \frac{18.9q}{\Delta}$, or the greater the molecular

weight the smaller will be the depression Δ for a given number of grams, q , of substance per 100 grms. of water. It follows also that for a given substance (i.e., when M is constant) the fraction q/Δ is also constant and equal to $M/18.9$. With other solvents (besides water) the constant, C , varies according to their properties (i.e., with t and w) ; thus, for benzene, C_6H_6 ($t=55^\circ$, $w=30$) it is about 50, for nitrobenzene about 70, for acetic acid about 39, &c. Extreme accuracy in the determination of the constant C cannot be expected, because the above relations are best seen in very dilute solutions, when the small amount of depression is difficult to determine. But as the cryoscopic method is only used in the laboratory to discover whether the molecular weight of the substance dissolved is M or some multiple of it, $2M$, $3M$, &c., a simple approximation to the true value is most important, especially for substances which are not at all volatile or which decompose when volatilised, more particularly as the value of M given by the cryoscopic method corresponds to low temperatures near the freezing-point of the solvent.

As an example we will again take a solution of ordinary sugar ($C_{12}H_{22}O_{11}$). P. D. Chrustchoff (1902) determined the depression of such solutions with a very sensitive electrical thermometer, and obtained the following results :—

Sugar in 100 grams of solution.	Sugar per 100 grams of Water. q	Observed Depression. Δ
0.998 gram	1.008 gram	0.0576°
2.081 „	2.125 „	0.1182°
4.302 „	4.495 „	0.2462°

According to these data :

$\frac{q}{\Delta}$	$C = \frac{\Delta M}{q}$	$M = 18.9q/\Delta$
17.50	19.55	330.8
17.98	19.03	339.7
18.26	18.74	344.9

Thus the molecular weight of sugar calculated from the depression is nearly the actual value (342.2), and if there be a slight difference (less than $3\frac{1}{2}$ per cent.) it is not sufficient to double or halve it. And this proves that sugar (even at low temperatures, when the molecules of many substances become more complex) has the same molecular weight as is directly deduced from its composition and reactions.

Thus depression gives the possibility of proving that the molecule of peroxide of hydrogen, for instance, is composed of H_2O_2 and not HO , that the molecules of oxygen, O_2 , chlorine, Cl_2 , and bromine, Br_2 , contain two atoms, as is also seen from their densities in a gaseous state ; that the saccharine body, raffinose, has a molecular formula, $C_{18}H_{32}O_{16}$ (according to Loiseau and Scheibler), and not $C_{36}H_{64}O_{32}$, as was formerly thought ; that many metals, judging by the depression of their dilute solutions (alloys) in Na, Sn, Bi, Cu, and Pb, generally (Heycock and Neville), contain one atom in their molecules, as is seen also from the vapour densities of certain of them (Cd, Hg, &c.)—Ramsay came to the same conclusion by determining the vapour pressures of their mercury solutions ; that the molecules of sulphur and phosphorus are complex both in solutions and in a state of vapour (see Chaps. XIX. and XX.), &c. One of the advantages of the cryoscopic method is that it gives an easy means of determining the polymerisation or complexity of molecules of similar composition. As an example may be cited citraconic, itaconic, and mesaconic acids, all having the same composition, $C_6H_6O_4$. It might have been thought that the difference between them lay, at least in part, in the polymerisation of their molecules, but Paterno and Nasini showed that solutions of all three acids of equal concentration exhibit a similar depression, so that the cause of the differences in their properties was necessarily due to true isomerism, i.e., to a difference in the structure or distribution of the atoms in the molecules. This was also confirmed by other chemical relations of these acids.

Raoult (1880–1885) showed that the rise of the boiling-point of solutions (i.e., the difference D between the boiling-points of the solution and of the solvent) and the relative fall of vapour pressure (i.e., the quotient obtained by dividing the difference between the vapour pressure of the solvent and of the solution by that of the solvent) also essentially

follow the same regularity as the depression,^{27a} and therefore give a means for directly determining the molecular weight.

The extreme and very remarkable simplicity in the relations between the variation of the osmotic pressure and depression (and other properties) of solutions with the amount (q grms. per 100 grms. of the solvent) of the substance dissolved and its molecular weight (M) ceases when we pass to saline substances (acids, bases, salts), and especially to their aqueous solutions, which are capable of transmitting an electric current (electrolytes). In the case of depression, for instance, we then obtain, not a constant (for a given solvent) value (C), but magnitudes which

^{27a} From the fact that solutions having similar osmotic pressures and depressions give a similar rise in the boiling-point and one and the same vapour pressure of the solvent, it follows that the dependence on the degree of concentration and molecular weight can be expressed in terms of D as well as of Δ , thus :

$$\frac{D}{q} M = C_2 = \frac{0.02(273 + t_1)^2}{w_1},$$

where C_2 is the constant for a given solvent, t_1 its boiling-point, and w_1 its latent heat of evaporation. Thus, for water $t_1 = 100$, and $w_1 = 538$, and, therefore $C_2 = 5.17$. For instance, for sugar, where (see above) $q = 1.008$, D has the value 0.0153 (hence for water, D is nearly four times less than Δ). For alcohol, C_2 is about 11.5° , for ether, nearly 21° , for acetic acid nearly 25° , for chloroform nearly 36° , and so on. Without going into details (which may be found in works on physical chemistry) we may state that as regards the fall of vapour pressure it follows the expression (Raoult, van't Hoff):

$$\frac{f - f_1}{f} \cdot \frac{M}{q} = C_3 = 0.02d,$$

where f is the vapour pressure (at a given t) of the solvent, f_1 the vapour density of the solution containing q grms. of the substance dissolved per 100 grms., M the molecular weight of the substance dissolved, d the vapour density of the solvent (density of hydrogen = 1) near its boiling-point in a state of saturation. Therefore C_3 is nearly 0.19 for water, 0.8 for CS_2 , 1.3 for CHCl_3 , and 1.5 for CH_3I , &c. In the case of acetic acid, $\text{C}_2\text{H}_4\text{O}_2$, the density of its superheated vapour is about 30, but when saturated at the ordinary temperature it is about 48, and therefore C_3 is about 0.96 for its solutions (Raoult and Recoura, 1890).

I think it not superfluous to mention here that the constant C obtained for the depression of different liquids (when the solvent crystallises out) has values for the majority of solvents equal to nearly 63 per cent. of their molecular weights. For instance, for benzene $C = 50$, and the molecular weight = 78, for acetic acid $C = 39$ and the molecular weight 60; but for water there is a different ratio, for $C = 18.9$ and the molecular weight = 18. This apparently shows that the molecules of water may be one and a half time as complex at low temperatures as in a state of vapour, and that a portion of the molecules become associated or polymerised. Researches on the surface tension of liquids (Eotvos, Ramsay and Shields, Rose Innes) determined by the magnitude of the capillary constant (Chap. I., note 11) and its variation with the temperature lead to the same conclusion (this subject, however, belongs to the province of physical chemistry). These researches show that the molecules of certain liquids have the same weight as in a state of vapour (CS_2 , C_6H_6 , &c.), whilst in others, including water, the molecule is associated or enlarged. In the case of water it is found that at low temperatures the molecule is more complex to the extent of $1\frac{1}{3}$ (Rose Innes), or maybe three times (Ramsay and Shields). Further details must be sought in works on physical chemistry, all the more so since no direct relation has yet been discovered between the association of the molecules of water and its chemical reactions at different temperatures (note 27).

either distinctly rise or fall with the dilution of the solution, and are generally greater than those given by solutions not capable of conducting an electric current, and which moreover vary for different substances dissolved. Therefore the observed results for such solutions do not give the true molecular weights, M , corresponding to the composition, but a certain value (M_1 , *generally* less than M , and the fraction $\frac{M}{M_1}$, designated by i) is found to be greater than unity (see Chapter I., notes 19 and 49).²⁸ The following examples show, on the one hand,

²⁸ Owing to the fact that the molecular weight of electrolytes, M_1 , calculated from the depression osmotic pressure, electro-conductivity, &c., of solutions, is found to be less than M , that is, found to be greater than unity, Arrhenius, Ostwald, Nernst, and many others hypothetically assume: (1) that a portion of the electrolyte in a solution is split up into **ions** (for instance, NaCl into Na and Cl, K_2SO_4 into K, K and SO_4); (2) that these ions produce the same action in solutions as whole molecules; and (3) that the measure of the decomposition into ions is determined by the degree of dilution, so that when the amount of water is considerable the value of i approaches the number of possible ions, but when the amount of water is less a portion of the molecules remains undecomposed, and therefore i is less for strong than for weak solutions. A whole series of remarkable scientific researches (increasing our knowledge of the chemistry of solutions) were devoted to the development of this **hypothesis of electrolytic dissociation** at the close of the nineteenth century, just as in former epochs of chemistry much labour was devoted, with the enrichment of science, to electro-chemistry, to the typical representation of the structure of substances, to the principles of thermo-chemistry and to chemical mechanics, and such-like theories, which gave their most valuable contributions to the treasure-house of our science, but which have yet been forsaken in their essential points and have played the part of 'working hypotheses,' suitable for a given period of the development of science, and although a means for prompting enquiry were yet found to be far from realities and were eventually abandoned. And such in my opinion is the hypothesis of electrical dissociation (see Chap. I., note 49), all the more so as it is at variance with many facts. And as it has so far not contributed anything to the purely chemical aspect of the theory of elements, I consider it superfluous to treat of it fully in this book, the more so as this subject is, owing to its novelty, generally considered in detail by most works on physical chemistry. The chief motive which gave rise to this hypothesis is the deviation from van't Hoff's and Raoult's laws exhibited by solutions of electrolytes, which give values for i greater than unity, that is, a molecular weight M_1 less than M (the chemical molecular weight), which might be taken to indicate a splitting up of the chemical molecules of the dissolved substance in such a solution. But at the same time the same physico-chemical researches gave evidence of discrepancies in a contrary direction, indicating the association of molecules, in the case of water (note 27a), alcohol, acetic acid, and other—more especially hydroxylic—solvents, so that the matter reduces itself to this, that certain classes of chemical compounds (saline, hydroxylic) exhibit deviations from the normal behaviour proper to such indifferent bodies as the hydrocarbons and the majority of organic compounds. I think that the best interpretation of all these (abnormal) phenomena can only be obtained by increasing the number of researches (especially on the depression and fall of vapour pressure) with other solvents than water, like those made by Professor Walden (1901, Riga) on solutions in liquid sulphurous anhydride, SO_2 . By employing the method of the rise of the boiling-point, and using the constant $C_2 = 15.0$ for SO_2 (non-conductors gave i nearly equal to 1, although C_2 was calculated as shown in the preceding note from the boiling-point and latent heat of evaporation of SO_2), Walden showed that, among the electrolytes, many substances give values of i nearly equal to 1 (or tending towards unity) in very dilute solutions; for instance RbI and $N(CH_3)_3HCl$, while other saline compounds of the composition $N(CH_3)_4Cl$,

how far the results of different observers agree in respect to the value of C (if M be taken according to the chemical composition), and, on the other hand, that C not only varies with the amount q , but also with the properties and composition of the substance dissolved. The last column but one gives the value of $i = M/M_1 = M \frac{18.9q}{\Delta}$, in order to show that, with electrolytes in aqueous solution, i is generally greater than unity and varies (like C) with q and the substance taken.^{28a} In each case the concentration of the solution increases as we descend the table. The last column gives n , or the number of molecules of the substance dissolved per 100 molecules of water, that is, $n = 18q/M$, as this expresses the concentration of the solution very clearly.

For common salt NaCl ($M=58.5$), according to Pickering's (1892) observations, we obtain :

Salt per 100 grams of Water. q	Depression. Δ	$\frac{\Delta M}{q}$ C	$\frac{C}{18.9} = \frac{M}{M_1}$ i	Number of molecule per 100 H_2O . n
0.0325 gram	0.0177°	31.8	1.7	0.01
0.0975 „	0.0598°	35.9	1.9	0.03
0.1625 „	0.0992°	35.7	1.9	0.05
0.3250 „	0.1958°	35.3	1.9	0.10
1.6250 „	0.9544°	34.3	1.8	0.50

$\text{N}(\text{C}_2\text{H}_5)_4\text{I}$, and even $\text{S}(\text{CH}_3)_3\text{I}$, in solutions of SO_2 , give values of i either slightly greater than 1 or of such magnitude that they exceed 1 on further dilution. For some of the electrolytes, for instance, KI , KCNS , &c., i is distinctly less than 1, but in all these cases it increases as the solution becomes more dilute, so that i may be assumed to approximate to 1, for the limit of dilution. Walden only obtained $i=2.05$ for the crystalline compound of picric acid with β -naphtol, although the solution does not conduct an electric current, and it is difficult to suppose that decomposition takes place in the act of solution, because picric acid is insoluble in liquid SO_2 . Moreover (as with aqueous solutions) the addition of the solvent to these solutions causes the value of i sometimes to fall and sometimes to rise, and the electro-conductivity of the solutions of some salts in SO_2 is greater than that of their aqueous solutions, while for others it is less. Such facts as these, which are at variance with the hypothesis of electrolytic dissociation, may be explained, although most arbitrarily, in the sense of this hypothesis by the supposition that association takes place simultaneously with the dissociation, but it appears to me far more natural to acknowledge that exceptions to van't Hoff's law of various kinds do undoubtedly exist and are most frequently met with among electrolytes, and that so far we can only partially distinguish a uniformity in a series of phenomena in passing from one property of a solution to another, but that the internal cause of the anomalies is not yet known. If the cause of these anomalies be sought in the chemism of electrolytic solutions, we must first ask what is the effect of the reaction of the solvent on the substance dissolved. Is there not the beginning of an act of combination and of double decomposition like the action of water on a salt: $\text{MX} + \text{H}_2\text{O} = \text{MHO} + \text{MX}$? And are not the exceptions to the law exhibited by saline substances due to the fact that these substances are capable of 'instantaneous' (see Chap. I., note 49 (Kahlenberg's experiment) and in general energetic chemical reaction?

^{28a} The normal value of i for non-conductors is approximately 1; for instance, for the three solutions of sugar, judging from the above, $i=1.035$, 1.008 , and 0.992 .

The more exact observations made by Chrustchoff (1902) with the electrical thermometer agree with the above in their essential features, as the following table shows :

q	Δ	C	i	n
0.0927 gram	0.0544°	34.33	1.82	0.0302
0.1853 „	0.1082°	34.16	1.81	0.0605
0.3751 „	0.2190°	34.15	1.81	0.1225
0.7559 „	0.4420°	34.20	1.81	0.2468
1.4940 „	0.8608°	33.71	1.78	0.4877

It is seen that the value of C for dilute aqueous solutions of NaCl remains almost constant as the dilution increases, and gives $i=1.8$ (nearly) or a molecular weight, M_1 , of about 32.5. With strong solutions of NaCl the value of i increases and even exceeds 2. For instance, the solution containing 20 per cent. of salt ($q=25.0$) forms ice at -17.6° (De Coppet), i.e., $\Delta=17.6$, and therefore $C=41.2$ and $i=2.2$.^{28b} The solutions of KCl (and many other salts) closely resemble those of NaCl in their molecular depression, but many salts, even in dilute solution, exhibit a rapid increase of the molecular depression C as they become more dilute, and therefore with them the value of i increases with the amount of water. Sulphate of potassium, K_2SO_4 ($M=174.3$), is an instance in question. According to Chrustchoff :

q	Δ	C	i	$n = q \times 0.1031$
0.2798	0.0808°	50.69	2.66	0.0288
1.0941	0.2760°	43.97	2.33	0.1128
4.6096	1.0198°	38.56	2.04	0.4752

A similar increase of C and i with the degree of dilution with water is seen in many other solutions, for instance, in Chrustchoff's researches on $Pb(NO_3)_2$.²⁹

^{28b} This suffices to show that although i frequently increases and approaches the value 2, or in general a whole number, as the dilution of a solution of an electrolyte increases, still it is not a universal phenomenon, as is seen, for example, from Walden's (note 28) data. And this, and much more, undermines the hypothesis of electrolytic dissociation which is upheld by many chemists and physicists, only because of its simplicity and the ease with which it serves for constructing many new supplementary hypotheses. It seems to me that this hypothesis (of electrolytic dissociation) will in time occupy a position in the history of our science similar to that long ago accorded to phlogiston. Phlogiston had its numerous partisans who contributed much to science, although they pleaded for a false hypothesis.

²⁹ But in the case of sulphuric acid, the rise of C and i proceeds, starting with the solution containing about $2\frac{1}{2}$ per cent., in both directions, that is, on the addition of

Thus, within the limits of dilute solutions, C and i for a given electrolyte either remain almost constant or increase (this is most frequent), or in some cases decrease as the degree of dilution increases. This proves the evident complexity of the phenomenon and obliges us to look for like cases in other variations exhibited by solutions when diluted with water, and this forms one of the problems of modern physico-chemical research. And it is particularly instructive to note that the value of i in many instances of the solution of chemically similar electrolytes (for instance, KCl and $NaCl$) exhibits an analogy and dependence on the composition, while in other cases this is not observed. Thus, with sulphuric acid i is less than 2, and in the extreme limit of dilution apparently tends to approximate to the value 2; with sulphate of potassium i is greater than 2; with sulphate of magnesium (and in general RSO_4) it only slightly exceeds 1, which is also the case with $HgCl_2$ and certain other electrolytes. These instances illustrate the great complexity of the phenomena going on in the solution of saline substances. Consequently even dilute solutions of the electrolytes (in contradistinction to non-conductors) exhibit in their depression (osmotic pressure, vapour pressure, &c.) evident deviations from the laws of Raoult, van't Hoff, &c., for they evince a dependence not on the molecular weight alone, but also on the individual peculiarities of their composition.

Still it is found that certain of the properties of dilute solutions of the electrolytes are not so much determined by the individual properties of the component elements as by the molecular weight of the substance in solution, as illustrated by the vapour pressure of all substances and the osmotic pressure, depression, &c., of non-conductors. For instance, the specific gravity of corresponding (for example, chlorides) salts in dilute solutions, as is seen from the fact that solutions of the composition $RCl_n + 200H_2O$ (i.e., containing the molecular weight in grams of the salt RCl_n to 3,600 grams of water) exhibit a gradual rise in

either water or acid, as is seen from the very exact determinations of Chrustchhoff ($H_2SO_4, M = 98.08$):

q	Δ	C	i	$n = q \times 0.1835$
0.7065	0.2526°	35.07	1.85	0.1296
1.4354	0.4836°	33.04	1.75	0.2634
2.9444	0.9188°	31.61	1.67	0.5403
4.2494	1.3852°	31.97	1.69	0.7798

A like behaviour (minimum) of i is known for solutions of $BaCl_2$, $CaCl_2$, &c. (Arrhenius Pickering).

specific gravity with a rise in the molecular weight of the salt dissolved :—

	Molecular weight.	Sp. gr. at 15°.
HCl	36·5	1·0041
NaCl	58·5	1·0106
KCl	74·5	1·0121
BeCl ₂	80	1·0138
MgCl ₂	95	1·0203
CaCl ₂	111	1·0236
NiCl ₂	130	1·0328
ZnCl ₂	136	1·0331
BaCl ₂	208	1·0489

Thus not only in vapours and gases, but also in dilute solutions of solid and liquid substances, we see that if not all, still many properties are wholly dependent upon the molecular weight and not upon the quality of a substance, and that this gives the possibility of determining the weights of molecules by studying these properties (for instance, the vapour density, depression of the freezing-point, &c.). It is apparent from the foregoing that even the physical and still more so the chemical properties of homogeneous substances, especially solids and liquids, do not depend exclusively upon the weights of their molecules, but that many are in definite (see Chapter XV.) dependence upon the nature and weights of the atoms of the elements entering into their composition, and are determined by their individual peculiarities. Thus the density of solids and liquids (as will afterwards be shown) is chiefly determined by the weights of the atoms of the elements entering into their composition, inasmuch as dense elements (in a free state) and compounds are only met with among substances containing elements with large atomic weights, such as gold, platinum, and uranium. And these elements themselves, in a free state, are the heaviest of all elements. Substances containing such light elements as hydrogen, carbon, oxygen, and nitrogen (like many organic substances) never have a high specific gravity; in the majority of cases it scarcely exceeds that of water. The density generally decreases with the increase in the amount of hydrogen, which is the lightest element, and a substance is often obtained lighter than water, but all these relations are more complex than those exhibited by the vapour density. The refractive power of substances also depends entirely on the composition and the properties of the component elements.^{29a} The history of chemistry presents a

^{29a} With respect to the optical refractive power of substances, it must first be observed that the coefficient of refraction is determined by two methods: (*a*) either all the data are referred to one definite ray—for instance, to the Fraunhofer (sodium) line D

striking example in point—Newton foresaw from the high refractive index of the diamond that it would contain a combustible substance, since so many combustible oils have a high refractive power. We shall afterwards see (Chapter XV.) that many of those properties of substances which are in direct dependence not upon the weight of the molecules but upon their composition, or, in other words, upon the properties and quantities of the elements entering into them, exhibit a peculiar (periodic) dependence upon the atomic weights of the elements; that is, the mass (of molecules and atoms), proportional to the weight, determines the properties of substances as (with the distance) it also determines the motions of the heavenly bodies. The mass (weight) of

of the solar spectrum—that is, to a ray of definite wave-length, and often to that red ray (of the hydrogen spectrum) whose wave-length is 656 millionths of a millimetre; (*b*) or else Cauchy's formula is used, showing the relation between the coefficient of refraction and dispersion to the wave-length, $n = A + \frac{B}{\lambda^2}$, where A and B are two constants varying

for every substance but constant for all rays of the spectrum, and λ is the wave-length of that ray whose coefficient of refraction is n . In the latter method the investigation usually concerns the magnitudes of A, which are independent of dispersion. We shall afterwards cite the data, investigated by the first method, by which Gladstone, Landolt, and others established the conception of the refraction equivalent.

It has long been known that the **coefficient of refraction** n for a given substance decreases with the density D, so that the magnitude $(n-1) \div D = C$ is almost constant for a given ray (having a definite wave-length) and for a given substance. This constant is called the *refractive energy*, and its product with the atomic or molecular weight of a substance the *refraction equivalent*. The coefficient of refraction of oxygen is 1.00021, that of hydrogen 1.00014, their densities (referred to water) being 0.00143 and 0.00009, and their atomic weights, O = 16, H = 1; hence their refraction equivalents are 2.4 and 1.6 respectively. Water contains H_2O ; consequently the sum of the refraction equivalents is $(2 \times 1.6) + 2.4 = 5.6$. But as the coefficient of refraction of water = 1.331, its refraction equivalent is 5.958, or nearly 6. Comparison shows that the sum of the refraction equivalents of the atoms forming compounds (or mixtures) is approximately equal to the refraction equivalent of the compound. The researches of Gladstone, Landolt, Kannonikoff, Brühl, and others give the refraction equivalents of the elements determined from the composition (and chemical structure) of their compounds. The refraction equivalents of many elements could only be calculated from the solutions of their compounds. The composition of a solution being known, it is possible to calculate the refraction equivalent of one of its component parts, those for all its other components being known, and taking the sum of their equivalents as equal to the equivalent for the compound. The results are founded on the acceptance of a law which cannot be strictly applied. Nevertheless the representation of the refraction equivalents gives an easy means for directly, although only approximately, obtaining the coefficient of refraction from the chemical composition of a substance. For instance, from the composition of carbon bisulphide, CS_2 , and its density, 1.27, we find its coefficient of refraction to be 1.618 (because the refraction equivalent = $5 + 2 \times 16 = 37$, if $C = 5$ and $S = 16$), which is very near the actual figure. It is evident that in the above representation compounds are looked on as simple mixtures of atoms, and the physical properties of a compound as the sum of the properties present in the elementary atoms forming it. If this representation of the presence of simple atoms in compounds had not existed, the idea of combining by a few figures a whole mass of data relating to the coefficient of refraction of different substances could hardly have arisen. For further details on this interesting subject see works on physical chemistry.

the molecules determines, as we saw, many of the physical and chemical properties of substances, starting with their vapour densities and the amount entering into reaction, while the mass (weight of the atom) of the elements composing the molecule determines, as we shall afterwards see, many other chemical and physical properties of substances. The dependence of the visible properties on the masses of invisible molecules and atoms forms one of the greatest acquisitions of our science.³⁰

³⁰ It must be remembered, however, that the conception of mass or quantity of ponderable matter has remained, from the time of Newton and Galileo, in many respects obscure, and most important results for natural science may be expected from researches (and therefore hypotheses) on the attractions evidenced by masses of matter.

CHAPTER VIII

CARBON AND THE HYDROCARBONS

It is necessary to clearly distinguish between the two closely allied terms, charcoal and carbon. Charcoal is well known to everybody, although it is no easy matter to obtain it in a chemically pure state. Pure charcoal is a simple, insoluble, infusible, combustible substance produced by heating organic matter, and has the familiar aspect of a black mass, devoid of any crystalline structure, and completely insoluble. **Charcoal is a substance** possessing a peculiar combination of physical and chemical properties. This substance, while in a state of ignition, combines directly with oxygen; in organic substances it is found in combination with hydrogen, oxygen, nitrogen, and sulphur. But in all these combinations there is no real charcoal, in the same way as there is no ice in steam. What is found in such combinations is termed **carbon**—that is, **an element** common to charcoal, to those substances which can be formed from it, and also to those substances from which it can be obtained. Carbon may take the form of charcoal, but occurs also as diamond and as graphite. Truly no other element has such a wide terminology. Oxygen is always called 'oxygen,' whether it is in a free gaseous state, or in the form of ozone, or as oxygen in water, nitric acid, or carbonic anhydride. But here there is some confusion. It is evident that in water there is no oxygen in a gaseous form, such as can be obtained in a free state, and no oxygen in ozone, but a substance which is capable of producing oxygen, ozone, and water. As an element, oxygen possesses a known chemical individuality, and exerts an influence on the properties of those combinations into which it enters. Hydrogen gas is a substance which reacts with difficulty, but the element hydrogen represents in its combinations an easily displaceable component part. Carbon may be considered as an atom of carbon matter, and charcoal as a collection of such atoms forming a whole substance, or mass of molecules of the substance. The accepted atomic weight of carbon is 12, because that is the least quantity of carbon which enters

into combination in molecules of its compounds ; but the weight of the molecules of charcoal is probably very much greater. The molecular weight is unknown, because charcoal is capable of but few direct reactions, and those only occur at a high temperature (when the weight of its molecules probably changes, as does that of ozone when it changes into oxygen), and it does not turn into vapour and has no solvent.

Carbon exists in nature, both in a free and a combined state, in most varied forms and aspects. Carbon in a free state is found in at least *three* different forms, namely, charcoal, graphite, and the diamond. In a combined state it enters into the composition of what are called **organic substances**—a multitude of substances found in all plants and animals. It exists as carbonic anhydride both in air and in water, and in the soil and crust of the earth as salts of carbonic acid and as organic remains.

The variety of the substances of which the structure of plants and animals is built up is familiar to all. Wax, oil, turpentine, and tar, cotton and albumin, the tissue of plants and the muscular fibre of animals, tartaric acid and starch, all these and many other substances entering into the composition of the tissues and juices of plants and animals are carbon compounds.¹ The class of carbon compounds is so

¹ **Wood** is the non-vital part of ligneous plants, the vital part of ordinary trees being situated between the bark and the lignine. Every year a layer of lignine is deposited on this part by the juices which are absorbed by the roots and drawn up by the leaves, so that the age of trees may be determined by the number of lignine layers deposited. The woody matter consists principally of fibrous tissue on to which the lignine or so-called incrusting matter has been deposited. The tissue has the composition $C_6H_{10}O_5$, the substance deposited on it containing more carbon and hydrogen and less oxygen. This matter is saturated with moisture when the wood is in a fresh state. Fresh birch wood contains about 31 per cent. of water, lime wood 47 per cent., oak 35 per cent., pine and fir about 37 per cent. When dried in the air the wood loses a considerable quantity of water, and not more than 19 per cent. remains. By artificial means this loss of water may be increased. If water be driven into the pores of wood it sinks, as the lignine of which it is composed has a density of about 1.6. One cubic centimetre of birch wood does not weigh more than 0.901 gram, fir 0.894, lime wood 0.817, poplar 0.765, when in a fresh state; when in a dry state birch weighs 0.622, pine 0.550, fir 0.355, lime 0.430, guaiacum 1.342, and ebony 1.226 gram per c.c. On one hectare (2.7 acres) of woodland in the temperate zone the yearly growth attains 3,000 kilograms (or about 3 tons) of wood, but rarely reaches as much as 5,000 kilos. (of stems and roots, not including small branches and leaves). The average chemical composition of wood dried in air may be expressed as follows:—Hygroscopic water 15 per cent., carbon 42 per cent., hydrogen 5 per cent., oxygen and nitrogen 37 per cent., ash 1 per cent. Wood parts with its hygroscopic water and begins to decompose at 150° , and at about 300° it gives a brown, brittle, so-called red charcoal; above 350° black charcoal is produced. As the 5 per cent. of hydrogen contained in wood requires for its combustion about forty parts by weight of oxygen, which is present to the amount of about 37 per cent., all that burns of the wood is the carbon which it contains, 100 parts of wood only giving out as much heat as forty-two parts of charcoal, and therefore it would be far more profitable to use charcoal for heating purposes than wood, if it were possible to obtain it in such quantities as correspond with its percentage ratio—that is, forty parts per 100 parts of wood.

vast that it forms a separate branch of chemistry, known under the name of organic chemistry—that is, the chemistry of carbon compounds, or, more strictly, of the hydrocarbons and their derivatives.

Generally, however, the quantity produced is far less, not more than 30 per cent., because part of the carbon is given off as gas, tar, and other volatile substances. If wood has to be transported great distances, or if it is necessary to obtain a very high temperature by burning it, even as little as 25 per cent. of charcoal from 100 parts of wood may be advantageous. Charcoal (from wood) develops on burning 8,000 heat units, whilst wood dried in air does not develop more than 3,400 units, so that one part of charcoal gives as much heat as $2\frac{1}{2}$ parts of wood. As regards the temperature of combustion, it is far higher with charcoal than with wood, because burning wood gives, besides the carbonic anhydride which is also formed together with charcoal, a large proportion of water, the evaporation of which requires a considerable amount of heat.

The composition of the **growing parts** of plants, the leaves, young branches, shoots, &c., differs from the composition of the wood in that these vital parts contain a considerable quantity of sap which contains much nitrogenous matter (in the wood itself little of this exists), mineral salts, and a large amount of water. Let us take, for example, the compositions of clover and pasture hay in the green and dry states; in green clover there is about 80 per cent. of water and 20 per cent. of dry matter, about 3·5 of which is nitrogenous albuminous matter, about 9·5 soluble, and about 5 insoluble non-nitrogenous matter, and about 2 per cent. of ash. In dry clover or clover-hay there is about 15 per cent. of water, 13 per cent. of nitrogenous matter, about 70 per cent. of cellulose and other non-nitrogenous carbohydrates, and 7 per cent. of ash. This composition shows the difference existing between the nutritive properties of wood and the substances mentioned. These latter serve as food for animals, because they contain those substances which are capable

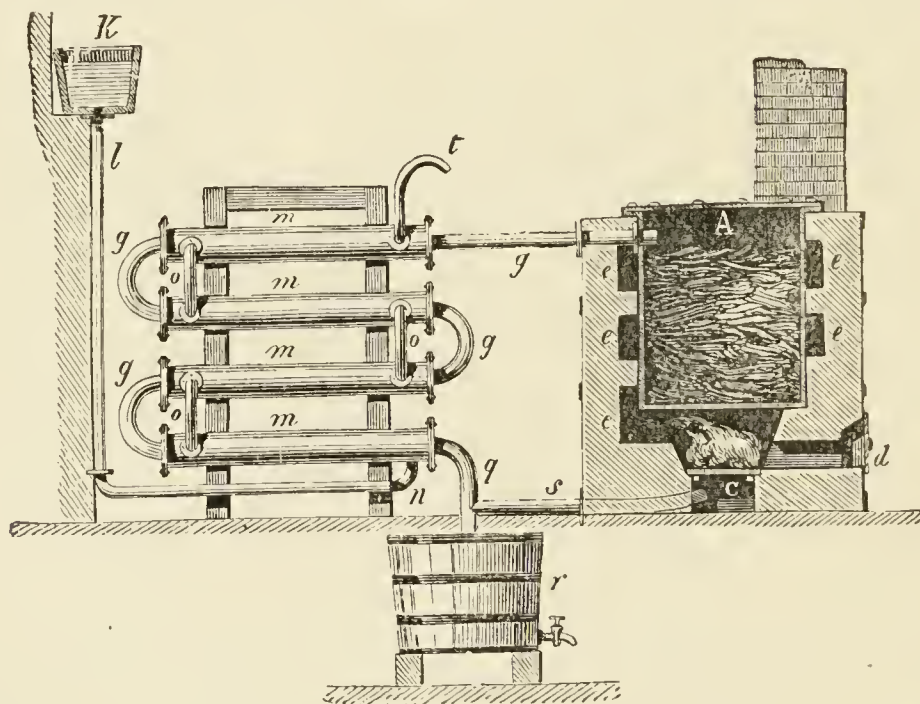


FIG. 65.—Apparatus for the dry distillation of wood. The retort *a* containing the wood is heated by the flues *c e*. The steam and volatile products of distillation pass along the tube *g* through the condenser *m*, where they are condensed. The form, distribution, and dimensions of the apparatus vary.

of being dissolved (entering into the blood) and of forming the bodies of animals; such substances are proteids, starch, &c. Let us remark here that with a good harvest an acre of land gives in the form of grass as much (and even more) organic substance in a year as it yields in the form of wood.

Dry wood is capable of giving, on **dry distillation**, besides 25 per cent. of charcoal and 10 per cent. or more of tar, 40 per cent. of watery liquid, containing acetic acid and wood spirit, and about 25 per cent. of gases, which may be used for heating or lighting purposes, because they do not differ from ordinary illuminating gas, which can indeed be obtained

If any one of these organic compounds be strongly heated without free access of air—or, better still, in a vacuum—it decomposes with more or less facility. If the supply of air be insufficient, or the temperature too low for combustion (see Chapter III.), and if the first volatile products of transformation of the organic matter are subjected to condensation (for example, if the door of a stove be opened), an *imperfect* combustion takes place, and **smoke**, with charcoal or soot, is formed.² The nature of the phenomenon, and the products arising from

from wood. As wood-charcoal and tar are valuable products, in some cases the dry distillation of wood is carried on principally for producing them. For this purpose those kinds of woods are particularly suitable which contain resinous substances, especially coniferous trees, such as the fir, pine, &c.; birch, oak, and ash give much less tar, but on the other hand they yield more aqueous liquor. The latter is used for the manufacture of wood spirit, CH_4O , and acetic acid, $\text{C}_2\text{H}_4\text{O}_2$. In such cases the dry distillation is carried on in stills. The stills are nothing more than horizontal or vertical cylindrical retorts, made of boiler plate, heated with fuel and having apertures at the top and sometimes also at the bottom for the exit of the light and heavy products of distillation. The dry distillation of wood in stoves is carried on in two ways, either by burning a portion of the wood inside the stove in order to submit the remainder to dry distillation by means of the heat obtained in this manner, or by placing the wood in a stove the thin sides of which are surrounded with a flue leading from the fuel, placed in a space below. The first method does not give such a large amount of the liquid products of dry distillation as the latter. In the latter process there is generally an outlet below for emptying out the charcoal at the close of the operation. For the dry distillation of 100 parts of wood from forty to twenty parts of fuel are used.

In the north of Russia wood is so plentiful and cheap that this locality is admirably fitted to become the centre of a general trade in the products of its dry distillation, especially acetic acid. Coal (note 6), seaweed, turf, animal substances (Chap. VI.), &c., are also submitted to the process of dry distillation.

² The result of imperfect combustion is not only the loss of a part of the fuel and the production of smoke, which in some respects is inconvenient and injurious to health, but also a low flame-temperature, which means that a less amount of heat is transmitted to the object heated. Imperfect combustion is not only always accompanied by the formation of soot or unburnt particles of charcoal, but also by that of carbonic oxide, CO , in the smoke (Chap. IX.) which burns, emitting much heat. In works and factories where large quantities of fuel are consumed, many appliances are adopted to ensure perfect combustion, and to combat against such a ruinous practice as the imperfect combustion of fuel. The most effective and radical means consists in employing combustible gases (producer and water gases), because by their aid perfect combustion can be easily realised without a loss of heat-producing power and the highest temperature can be reached. When solid fuel is used (such as coal, wood, and turf), imperfect combustion is most liable to occur when the furnace doors are opened for the introduction of fresh fuel. The step furnace may often prove a remedy for this defect. In the ordinary furnace fresh fuel is placed on the burning fuel, and the products of the dry distillation of the fresh fuel have to burn at the expense of the oxygen remaining uncombined with the burnt fuel. Imperfect combustion is observed in this case also from the fact that the dry distillation and evaporation of the water of the fresh fuel lying on the top of that burnt lowers the temperature of the flame, because part of the heat becomes latent. On this account a large amount of smoke (imperfect combustion) is observed when a fresh quantity of fuel is introduced into the furnace. This may be obviated by constructing the furnace (or managing the stoking) in such a way that the products of distillation pass through the red-hot charcoal remaining from the burnt fuel. It is only necessary, in order to ensure this, to allow a sufficient quantity of air for perfect combustion. All this may be easily attained by the use of step fire-bars. The fuel is fed into a hopper and

it, are the same as those produced by heating, since that part which is in a state of combustion serves to heat the remainder of the fuel. The decomposition which takes place on heating a compound composed of carbon, hydrogen, and oxygen is as follows:—A part of the hydrogen is separated in a gaseous state, another part in combination with oxygen, and a third part separates in combination with carbon, and sometimes in combination with carbon and oxygen in the form of gaseous or volatile products, or, as they are also called, the products of dry distillation. If the vapours of these products are passed through a strongly heated tube, they are changed again in a similar manner, and finally resolve themselves into hydrogen and charcoal. Altogether these various products of decomposition contain a smaller amount of carbon than the original organic matter; part of the carbon remains in a free state, forming charcoal.³ It remains in that space where falls on to the fire-bars, which are arranged in the form of a staircase. The burning charcoal is below, and hence the flame formed by the fresh fuel is heated by the contact of the red-hot burning charcoal. Coke, charcoal, and anthracite burn without smoke, because they do not contain hydrogenous substances which furnish the products of dry distillation, but imperfect combustion may occur with them also; in that case the smoke contains carbonic oxide. Details on the subject of fuel and furnaces, &c., must be sought in works on chemical technology.

³ Under the action of air, organic substances are capable of oxidising to such an extent that all the carbon and all the hydrogen they contain will be transformed into carbonic anhydride and water. The refuse of plants and that of animals are subjected to such a change whether they slowly decompose and putrefy, or rapidly burn with direct access of air. But if the supply of air be limited, there can be no complete transformation into water and carbonic anhydride, and there will then be other volatile matters (rich in hydrogen), while charcoal must remain as a non-volatile substance. All animal and vegetable substances are unstable, and change at ordinary temperatures, particularly if water is present. It is therefore easy to understand that charcoal may in many cases be obtained through the transformation of substances entering into the composition of organisms, but that it is never found in a pure state.

However, water and carbonic anhydride are not the only products separated from organic substances. Carbon, hydrogen, and oxygen are capable of giving a multitude of compounds; some of these are volatile compounds, gaseous, soluble in water—they are carried off from organic matter, undergoing change without access of air. Others, on the contrary, are non-volatile, rich in carbon, unaffected by the action of natural agents. The latter remain in admixture with charcoal in the place where the decomposition takes place; such, for example, are tarry substances. The quantity of those bodies found mixed with the charcoal is very varied, and depends on the energy and duration of the decomposing agent. The annexed table shows, according to the data of Violette, those changes which wood undergoes at various temperatures when submitted to dry distillation by means of superheated steam.—

Temperature	Residue from 100 parts of alder wood	In 100 parts of the residual charcoal			
		C	H	O and N	Ash
150°	100·0	47·5	6·1	46·3	0·1
350°	29·7	76·6	4·1	18·4	0·6
1032°	18·7	81·9	2·3	14·1	1·6
1500°	17·3	95·0	0·7	3·8	1·7

the decomposition took place, in the shape of the black, infusible and non-volatile charcoal familiar to all. The earthy matter, ash and all non-volatile substances forming a part of the organic matter remain behind with the charcoal. The tar-like substances, which require a high temperature in order to decompose them, also remain mixed with the charcoal. If a volatile organic substance, such as a gaseous compound containing oxygen and hydrogen, be taken, the carbon separates when the vapour is passed through a tube heated to a high temperature. Organic substances when burning with an insufficient supply of air give off soot—that is, charcoal—proceeding from carbon compounds in a state of vapour, the hydrogen of which has, by combustion, been converted into water; thus, for instance, turpentine, naphthalene, and other hydrocarbons which are with difficulty decomposed by heat, readily yield carbon in the form of soot during combustion.

Wood charcoal is prepared in large quantities in a similar manner—that is, by the partial combustion of wood.⁴ In nature a similar process of carbonisation of vegetable refuse takes place in its transformation under water, as shown by the marshy vegetation which forms peat.⁵

⁴ The object of producing charcoal from wood has been explained in note 1. **Wood charcoal** is obtained in so-called stacks by partially burning the wood, or by means of dry distillation (note 1) without the access of air. It is principally manufactured for metallurgical processes, especially for smelting and forging iron. The preparation of charcoal in stacks has one advantage, and that is, that it may be done on any spot in the forest. But in this way all the volatile products of the dry distillation are lost. For charcoal burning, a pile or stack is generally built, in which the logs are placed close together, either horizontally, vertically, or inclined, forming a stack of from six to fifty feet in diameter, and even larger. Under the stack are several horizontal air passages, and in the middle an opening to let out the smoke. The surface of the stack is covered with earth and sods, in order to hinder the free passage of air and to concentrate the heat inside. When the stack is kindled, the pile begins to settle down by degrees, and it is then necessary to look after the turf casing and keep it in repair. As the combustion spreads throughout the whole pile, the temperature rises and real dry distillation commences. It is then necessary to stop the air holes, in order to prevent as far as possible unnecessary combustion. The essence of the process is, that part of the fuel burns and develops the heat required for subjecting the remainder to dry distillation. The charring is stopped when the products of dry distillation, which are emitted, no longer burn with a brilliant flame, but with the pale blue flame of carbonic oxide. Dry wood in stacks yields about one-fourth of its weight of charcoal.

⁵ When dead vegetable matter undergoes transformation in the air, in the presence of moisture and lower organisms, there remains a substance richer in carbon—namely, **humus**, black earth, or mould. In a dry state humus contains about 70 per cent. of carbon. The non-vital vegetable substance (ligneous tissue) first forms brown matter (ulmic compounds), and then black matter (humic substances), which are both insoluble in water; after this a brown acid is produced, which is soluble in water (apocrenic acid), and lastly a colourless acid also soluble in water (crenic acid). Alkali dissolves a part of the original brown and black substances, forming solutions of a brown tint (ulmic and humic acids) which sometimes communicate their colour to springs and rivers. The proportion of humus in soil generally has a direct influence on its fertility; first, because putrefying plants develop carbonic anhydride and ammonia, and yield the

In this manner were doubtless formed ⁶ the enormous masses of coal which, following the example set by England, are now utilised

substances forming the ashes of plants, which are necessary to vegetation; secondly, because humus is capable of attracting the moisture of the air and of absorbing water (twice its weight) and in this way keeps the soil in a damp condition, which is indispensable for nourishment; thirdly, humus renders the soil porous; and, fourthly, it renders it more capable of absorbing the heat of the sun's rays. On this account black earth is often possessed of most remarkable fertility. One object of manuring is to increase the quantity of humus in the soil, and any easily changeable vegetable or any animal matter (composts) may be used. The boundless tracts of black earth soil in Russia are capable of bestowing countless wealth on the country.

The origin and extent of black earth soil are treated in detail in Professor Dokouchaëff's works.

If those substances which produce humus undergo decomposition under water, less carbonic anhydride is formed, a quantity of marsh gas, CH_4 , is evolved, and the solid residue forms an acid humus found in large quantities in marshy places and called **peat**. Peat is especially abundant in the lowlands of Holland, North Germany, Ireland, and Bavaria. In Russia it is likewise found in large quantities, especially in the central districts. The old hard forms of peat resemble, in composition and properties, brown coal; the newest formations, as yet unhardened by pressure, form very porous masses which retain traces of the vegetable matter from which they have been formed. Dried (and sometimes pressed) peat is used as fuel. The composition of peat varies considerably with the locality in which it is found. When dried in air it does not contain less than 15 per cent. of water and 8 per cent. of ash; the remainder consists of 45 per cent. of carbon, 4 per cent. of hydrogen, 1 per cent. of nitrogen, and 28 per cent. of oxygen. Its heating power is about equivalent to that of wood. The **brown** earthy varieties of **coal** were probably formed like peat. In other cases they have a marked woody structure, and are then known as lignites. Brown coals present an intermediate stage between peat and coals.

⁶ Grass and wood, the vegetation of primeval seas and similar refuse of all geological periods, must have been in many cases subjected to the same changes as they now undergo—that is, under water they formed peat and lignites. Such substances, preserved for a long time underground, subjected to the action of water, compressed by the more recent strata formed above them, transformed by the separation of their more volatile component parts (peat and lignites, even in their last condition, still continue to evolve nitrogen, carbonic anhydride, and marsh gas), form **coal**. Coal is a dense homogeneous mass, black, with an oily or glassy lustre, or more rarely dull without any evident vegetable structure; this distinguishes it in appearance from the majority of lignites. The density of coal (not counting the admixture of pyrites, &c.) varies from 1.25 (dry bituminous coal) to 1.6 (anthracite, flameless), and even reaches 1.9 in the very dense variety of coal found in the Olonetzky Government (termed shungite), which according to the investigations of Professor Inostrantzeff may be regarded as the extreme member of the various forms of coal.

In order to explain the formation of coal from vegetable matter, Cagniard de la Tour enclosed pieces of dried wood in a tube and heated them to the boiling-point of mercury, when the wood was changed into a semi-liquid black mass, from which a substance exceedingly like coal separated. In nature the decomposition was in rare cases probably effected by heat alone; more generally it was effected by means of water and heat, but in either case the result should be almost the same.

The average composition of coal compiled from many analyses, disregarding the ash, is as follows: 84 parts of carbon, 5 parts of hydrogen, 1 part of nitrogen, 8 parts of oxygen, 2 of sulphur. The quantity of ash is on an average 5 per cent., but there are coals which contain a larger quantity, and naturally they are not so suitable for use as fuel. The **anthracites** form a remarkable variety of coals, giving no volatile products, or but a very small amount, as they contain but little hydrogen compared with oxygen. In

everywhere as the principal material for heating steam boilers, and in general for all purposes of heating and burning.⁷ Russia possesses many very rich coalfields, amongst which the Donetz district is most worthy of remark at the present day.⁸

the average composition of coal we saw that for 5 parts of hydrogen there were 8 parts of oxygen; therefore 4 parts by weight of the hydrogen are capable of forming hydrocarbons, because 1 part of hydrogen is necessary in order to form water with the 8 parts of oxygen. These 4 parts by weight of hydrogen can convert 48 parts of carbon into volatile products, because 1 part of hydrogen by weight is combined in these substances with 12 parts of carbon. The anthracites differ essentially from this: neglecting the ash, their average composition is as follows: 94 parts of carbon, 3 of hydrogen, and 3 of oxygen and nitrogen. According to the analyses of A. A. Voskresensky, the Grousheffsky anthracite (Don district) contains: C = 93.8, H = 1.7, ash = 1.5. So that the anthracites contain but little hydrogen capable of combining with the carbon to form hydrocarbons which burn with a flame. Anthracites are the oldest forms of coal. The newest and least transformed coals, which resemble some of the brown varieties, are the *dry* coals. They burn with a flame like wood, and leave a coke having the appearance of lumps of coal, half their component parts being absorbed by the flame (they contain much hydrogen and oxygen). According to Grüner, the remaining varieties of coal (gas coal, smithy coal, coking, and anthracite) form in all respects connecting links between the dry coals and the anthracites. These coals burn with a very smoky flame, and on being heated leave **coke**, which bears the same relation to coal as charcoal does to wood. The quantity and quality of the coke vary considerably with the different sorts of coal from which it is formed. In practice coals are most often distinguished by the properties and quantity of the coke which they give. In this particular the so-called bituminous coals are especially valuable, as even slack of this variety gives on dry distillation large spongy masses of coke. The best coking coals give 65 per cent. of dense caking coke. Such coal is very valuable for metallurgical purposes (see note 8). Besides coke, the dry distillation of coal produces gas (see further, illuminating gas), coal-tar (which gives benzene, carbolic acid, naphthalene, tar for artificial asphalt, &c.) and also an aqueous alkaline liquor (with wood and lignites the liquid is acid from acetic acid) which contains ammonium carbonate (see note 6).

⁷ In England the output of coal in 1850 was as much as 48 million tons, and in latter years it has risen to about 220 millions. The United States of America already exceed England in output, and the whole world produces yearly about 650 million tons of coal, of which about 25 million tons fall to the share of Russia. Thus the world consumes over half a milliard tons of coal a year, representing a value of not less than half a milliard pounds sterling. Coal thus forms, after corn, the most important article of commerce. Its chief demand is for the generation of mechanical power in steamers, railways, and manufactories, and also for the production of iron and other metals, and for heating purposes. As every horse-power (= 75 kilogrammetres per second) of a steam-engine uses up on the average more than 25 kilograms in 24 hours, or in a year (counting stoppages) as much as 5 tons, not less than 65 million horse-power must be at work in the world. For this reason coal serves as a criterion of the industrial development of a country. About 15 per cent. of the coal is used for the manufacture of cast iron, wrought iron, steel, and articles made of them.

⁸ The principal coal beds of Russia under exploitation are: The Don basin (1901, about 930 million poods; 62 poods = 1 ton), the Polish basin (Dombrovo and others), the Toula and Riazan beds of the Moscow basin, the Ural basin, the Caucasian (Kviboul, near Kutais), the Khirjhis steppes, the smithy coal basin (Government of Tomsk), the Sahaline, &c. The Polish and Moscow basins do not give any coking coals. The presence of every variety of coal (from the dry coal near Lisichansk on the Donetz to the anthracites of the entire south-east basin), the great abundance of excellent metallurgical coal (coking, see note 6) in the western part of the basin, its vast extent (as much as 25,000 sq. versts),

Judging from what has been already said, **soot** is finely divided charcoal separated during the imperfect combustion of the vapours and gases of carbonaceous substances rich in carbon. Specially prepared soot (lampblack) is very largely used as a black paint and a large quantity goes for the manufacture of printer's ink. It is prepared by burning tar, oil, natural gas, naphtha, &c. The quantity of organic and tarry matter remaining undecomposed in the charcoal depends on the temperature to which it has been submitted. Charcoal prepared at the lowest temperature still contains a considerable quantity of hydrogen and oxygen—even as much as 4 per cent. of hydrogen and 20 per cent. of oxygen. Such charcoal still preserves the structure of the substance from which it was obtained. Ordinary charcoal, for instance, in which the structure of the tree is still visible, is of this kind. On submitting it to further heating, a fresh quantity of hydrogen with carbon and oxygen (in the form of gases or volatile matter) may be separated, and the purest charcoal will be obtained on submitting it to the greatest heat.⁹ If it be required to prepare pure charcoal from soot, it is necessary to first wash it with alcohol and ether in order to remove the soluble tarry products, and then submit it to a powerful heat to drive off the impurities containing hydrogen and oxygen. Its porosity,¹⁰ bad conducting power for heat, capacity for

the proximity of the seams to the surface (the shafts are now from 20 to 150 fathoms deep, and in England and Belgium as deep as 500 fathoms), the fertility of the soil (black earth), the proximity of the sea (about 100 versts from the Sea of Azov) and of the rivers Donetz, Don, and Dneiper, the abundant seams of excellent iron ore (Korsan Mogila, Krivoy Rog, Soulin, &c.), copper ore, mercury ore (near Nikitovka, in the Bakhmouth district of the Ekaterinoslav Government), and other ores, the richest probably in the whole world, the beds of rock-salt (near the stations of the Stoupka and Brianzovka), the excellent clay of all kinds (china, fire-clay), gypsum, slate, sandstone, and other **wealth of the Don coal basin**, give complete assurance of the fact that, with the growth of industrial activity in Russia, this bountiful land of the Cossacks and New Russia will become the centre of the most extensive productive enterprise, not for the requirements of Russia alone, but for those of the whole world, because in no other place can be found such a concentration of favourable conditions.

⁹ As it is difficult to separate from the charcoal the admixture of ash—that is, the earthy matter contained in the vegetable substance used for producing charcoal—in order to obtain it in its purest condition it is necessary to use such organic substances as do not contain any ash, for example, completely refined or purified crystallised sugar, crystallised tartaric acid, &c.

¹⁰ The cavities in charcoal are the passages through which those volatile products formed at the same time as the charcoal have passed. The degree of porosity of charcoal varies considerably in different kinds of charcoal, and has a technical significance. The most porous charcoal is very light; a cubic metre of wood charcoal weighs about 200 kilograms. Many of the properties of charcoal which depend exclusively on its porosity and surface conditions are shared by certain other porous (contact) substances, and vary with the way it is prepared. The property which charcoal has of absorbing gases, liquids, and many substances in solution is a case in point. The densest kind of charcoal is formed by the action of great heat on sugar and other fusible substances.

absorbing the luminous rays (hence its blackness and opacity), and many other qualities, are familiar from everyday experience.¹¹ The specific gravity of charcoal varies from 1·4 to 1·9, and that it floats on water is due to the air contained in its pores. If charcoal is reduced to a powder and moistened with spirit, it immediately sinks in water.

The lustrous grey dense coke formed in gas retorts is also of this character. This dense coke collects on the internal walls of the retorts subjected to great heat, and is produced by the vapours and gases separated from the heated coal in the retorts. In virtue of its density such coke becomes a good conductor of the galvanic current and approximates to graphite. It is principally used in galvanic batteries. Coke, or the charcoal remaining from the imperfect combustion of coal and tarry substances, is also but slightly porous, brilliant; does not soil or mark paper, is dense, almost devoid of the faculty of retaining liquids and solids, and does not absorb gases. The light sorts of charcoal produced from charred wood, on the other hand, show this absorptive power in a most marked degree. This property is particularly developed in that very fine, friable charcoal prepared by heating animal substances such as hides and bones. **The absorptive power of charcoal** for gases is similar to the condensation of gases in spongy platinum. There is here evidently a case of the adherence of gases to a solid, precisely as liquids adhere to various solids. One volume of charcoal will absorb the following volumes of gases (charcoal is capable of absorbing an immense amount of chlorine, almost equal to its own weight):—

Saussure. Boxwood Charcoal		Favre. Cocoanut Charcoal		Heat emitted per gram of gas absorbed	
NH ₃	90	172	vols.	494	units
CO ₂	35	97	„	158	„
N ₂ O	40	99	„	169	„
HCl	85	165	„	274	„

The quantity of gas absorbed by the charcoal increases with the pressure, and is approximately proportional to it. The quantity of heat given out by the absorption nearly approaches that set free by the gas on dissolving, or on passing into a liquid condition.

Charcoal absorbs not only gases, but a number of other substances. For instance, alcohol which contains disagreeably smelling fusel oil, on being mixed with charcoal or filtered through it, loses most of the fusel oil. The practice of filtering substances through charcoal in order to get rid of foreign matters is often applied in chemical and manufacturing processes. Oils, spirits, various extracts, and vegetable and other solutions are filtered through charcoal in order to purify them. The bleaching power of charcoal may be tested by using various coloured solutions—such as aniline dyes, litmus, &c. Charcoal which has absorbed one substance to saturation is still capable of absorbing certain other substances. Animal charcoal, produced in a very finely divided state (and containing a certain amount of nitrogenous matter), especially by heating bones, is the best form for the purposes of absorption. Bone charcoal is used in large quantities in sugar works for filtering syrups and all saccharine solutions, in order to purify them, not only from colouring and odorous matter, but also from the lime which is mixed with the syrups in order to render them less unstable during boiling. The absorption of lime by animal charcoal very probably depends in a great degree on the presence of mineral constituents.

¹¹ Charcoal is a very bad conductor of heat, and therefore forms an excellent insulator or packing to prevent the transmission of heat. A charcoal lining is often made use of in crucibles for heating substances, as it does not melt, and resists a far greater heat than many other substances.

It is **infusible** in the furnace and even at the temperature of the oxyhydrogen flame. In the heat generated by means of a powerful galvanic current charcoal only softens but does not completely melt, and on cooling it is found to have undergone a complete change both in properties and appearance, and to present more or less of a transition towards graphite. The physical stability of charcoal is without doubt allied to its chemical stability. It is evidently a substance devoid of energy, for it is insoluble in all known liquids, and **at ordinary temperatures does not combine with anything**; it is an inactive substance, like nitrogen.¹² But these properties of charcoal change with a rise of temperature; thus, unlike nitrogen, charcoal, at a high temperature, combines directly with oxygen. This is well known, as charcoal burns in air. Indeed, not only does oxygen **combine with charcoal at a red heat**, but sulphur, hydrogen, silicon, and also iron and many other metals ^{12a} do so at a very high temperature—that is, when the molecules of the charcoal have reached a state of great instability—whilst at ordinary temperatures neither oxygen, sulphur, nor metals act on charcoal in any way. When burning in oxygen, charcoal forms carbonic anhydride, CO_2 , or in the presence of an excess of charcoal gaseous carbon monoxide, CO , whilst in the vapours of sulphur, carbon bisulphide, CS_2 , is formed; further iron and other metals, when acted on by carbon, form solid non-soluble carbides. At the great heat obtained by passing the galvanic current through carbon electrodes, charcoal combines with hydrogen, forming acetylene, C_2H_2 . Charcoal does not combine directly with nitrogen, but in the presence of metals and alkaline oxides, nitrogen is absorbed, forming a metallic cyanide, such, for instance, as potassium cyanide, KCN . In all respects the faculty of carbon for combining with oxygen is its most important property.

¹² The unalterability of charcoal under the action of atmospheric agencies, which produce changes in the majority of stony and metallic substances, is often made use of in practice. For example, charcoal is frequently strewn in boundary ditches. The surface of wood is often charred to render it durable in those places where the soil is damp and wood itself would soon rot. The chambers (or in some works towers) through which acids pass (for example, sulphuric and hydrochloric) in order to bring them into contact with gases or liquids, are filled with charcoal or coke, because at ordinary temperatures it resists the action of even the strongest acids.

^{12a} The carbides of Ca, Se, Ba are mentioned at the end of Chap. XIV., Al_4C_3 in Chap. XVII., note 3, &c. As regards the different carbides, Moissan, who obtained them by the action of charcoal on oxides under the influence of the heat of the voltaic arc, observed that water does not act on some of them (Fe_3C , Cr_3C_2 , Cr_4C_4 , Mo_2C , WC , VC , ZrC , TiC), whilst others—for instance, C_2Li_2 , C_2Ca (also Sr , Ba), Be_2C , CMn_3 , C_3Ur_2 —are decomposed with the evolution of hydrocarbons. Some of the carbides (of Au, Bi, Sn) do not dissolve carbon in the heat of the electric furnace, while others (of Cu, Ag, Pt) dissolve it to a greater or less extent under these conditions, but in the majority of cases deposit it as graphite on cooling. It must be mentioned that K_2C_2 and Na_2C_2 are easily decomposed by heat, and can only be obtained indirectly (see Chapter XII.).

Certain substances containing oxygen give up a part of it to charcoal at a relatively low temperature. For instance, nitric acid when boiled with charcoal gives carbonic anhydride and nitrogen peroxide. Sulphuric acid is reduced to sulphurous anhydride when heated with carbon. When heated to redness charcoal absorbs oxygen from water and a large number of the oxides. Even such oxides as those of sodium and potassium, when heated to redness, yield their oxygen to charcoal, although they do not part with it to hydrogen. Only a few of the oxides, like silica (oxide of silicon) and lime (calcium oxide), resist the reducing action of charcoal at the temperature produced by the combustion of charcoal itself, but they frequently react with it at the temperature obtained in the electric arc (3000° – 3500°). Thus lime, CaO , gives up its oxygen and forms carbon monoxide, and the metallic calcium set free combines with the excess of carbon at the temperature of the voltaic arc, and forms carbide of calcium, CaC_2 . Charcoal is capable of changing its structure and physical condition without undergoing any alteration in its essential chemical properties—that is, it passes into **isomeric** or **allotropic forms**. The two other particular forms in which carbon appears are the **diamond** and **graphite**. The identity of composition of these with charcoal is proved by burning equal quantities of all three separately in oxygen (at a very high temperature), when each gives the same quantity of carbonic anhydride—namely, 12 parts of charcoal, diamond, or graphite in a pure state, yield on burning 44 parts by weight of carbonic anhydride. The physical properties present a marked contrast; the densest sorts of charcoal only have a density of 1.8, whilst the density of graphite is about 2.3, and that of the diamond 3.5. A great many other properties depend on the density, for instance, combustibility. The lighter charcoal is, the more easily it burns; graphite burns with considerable difficulty even in oxygen, and the diamond burns only in oxygen and at a very high temperature. On burning, charcoal, the diamond, and graphite develop different quantities of heat. One part by weight of wood charcoal converted by burning into carbonic anhydride develops 8,080 heat units; dense charcoal separated in gas retorts develops 8,050 heat units; natural graphite, 7,800 heat units; and the diamond 7,770. The greater the density the less the heat evolved by the combustion of the carbon.¹³ Graphite is comparatively soft, and leaves a streak when

¹³ When subjected to pressure, charcoal loses a portion of its internal energy (heat); hence the densest form stands to the less dense in the same relation as a solid to a liquid, or as a compound to an element. From this the conclusion may be drawn that the molecules of graphite are more complex than those of charcoal, and those of the diamond still more so. The specific heat shows the same variation, and, as we shall see further on, the increased complexity of a molecule leads to a diminution of the specific

drawn over paper, &c. (whence its name from the Greek *γράφω*, I write), and is therefore employed for the manufacture of pencils.

By means of intense heat charcoal may be transformed into **graphite**. If a charcoal rod 4 mm. in diameter and 5 mm. long be enclosed in an exhausted receiver and the current from 600 Bunsen's elements, placed in parallel series of 100, be passed through it, the charcoal becomes strongly incandescent, partially volatilises, and is deposited in the form of graphite. If sugar be placed in a charcoal crucible and a powerful galvanic current passed through it, it is baked into a mass similar to graphite. If charcoal be mixed with wrought iron and heated, cast iron is formed, which contains as much as five per cent. of carbon. If molten cast iron be suddenly chilled, the carbon remains in combination with the iron, forming so-called white cast iron; but if the cooling proceeds slowly, the greater part of the carbon separates out in the form of graphite, and if such cast iron (so-called grey cast iron) be dissolved in acid, graphite is left as a residue. Graphite is met with in nature, sometimes in the form of large compact masses, sometimes permeating rocky formations like the schists or slates, and in fact is met with in those places which, in all probability, have been subjected to the action of subterranean heat.¹⁴ The graphite in cast iron, and sometimes also natural graphite, occasionally appears in a crystalline form in the shape of six-sided plates, but more often it occurs as a compact amorphous mass having the characteristic properties of the familiar black-lead pencil.¹⁵

heat. At ordinary temperatures the specific heat of charcoal is 0.24, that of graphite 0.20, and that of the diamond 0.147. For retort carbon Le Chatelier (1893) found that the product of the sp. heat and atomic weight varies, between 0° and 250°, according to the formula: $1.92 + 0.0077t$; and between 250° and 1,000°, it is $3.54 + 0.00246t$ (see Chapter XIV., note 4).

¹⁴ There are places where anthracite gradually changes into graphite as the strata sink. I myself had the opportunity of observing this gradual transformation in the valley of Aosta.

¹⁵ Pencils are made of graphite worked up into a homogeneous mass by disintegrating, powdering, and cleansing it from earthy impurities; the best kinds are made of completely homogeneous graphite sawn up into the requisite sticks. Graphite is found in many places. In Russia the so-called Siberian or Aliberoffsky graphite is particularly renowned; it is found in the Altai mountains near the Chinese frontier; in many places in Finland and likewise on the banks of the Little Tungouska, Sidoroff also found a considerable quantity of graphite. A large amount of graphite comes from Ceylon. Natural graphite always contains mineral impurities. When mixed with clay, graphite is used for making crucibles and pots for melting metals.

Like most forms of charcoal, graphite still contains a certain quantity of hydrogen, oxygen, and ash, so that in its natural state it does not contain more than 98 per cent. of carbon.

In practice, graphite is purified simply by washing it when in a finely ground state, by which means the bulk of the earthy matter may be separated. The process, proposed by Brodie, consists in mixing the powdered graphite with $\frac{1}{14}$ part of its weight of potas-

The **diamond** is a crystalline and transparent form of carbon. It is of rare occurrence in nature, and is found in the alluvial deposits of the diamond mines of Brazil, India, South Africa, &c.^{15a} It has also been found in meteorites. It crystallises in octahedra, dodecahedra, cubes, and other forms of the regular system.¹⁶ The efforts which have been made to produce diamonds artificially, although they have not been fruitless, have not as yet led to the production of large-sized crystals, because those means by which crystals are generally formed are inapplicable to carbon. Indeed, carbon in all its forms is insoluble at low temperatures, and deposits graphite from its solutions at higher temperatures under the ordinary pressure. Diamonds may, however, be obtained in the shape of minute crystals having the appearance of a black powder, but when viewed under the microscope appearing transparent, and possessing that hardness which is the peculiar characteristic of the diamond. This diamond powder is deposited on the negative

sium chlorate and heating the mixture with twice its weight of strong sulphuric acid until no more odoriferous gases are emitted; on cooling, the mixture is thrown into water and washed, the graphite being then dried and heated to a red heat, when it shrinks considerably in volume and forms a very fine powder, which is then washed. By acting on graphite several times with a mixture of potassium chlorate and nitric acid heated up to 60°, Brodie transformed it into a yellow insoluble acid substance which he called graphitic acid, having very nearly the composition $C_{11}H_4O_5$. The diamond remains unchanged when subjected to this treatment, whilst amorphous charcoal is completely oxidised. Availing himself of this possibility of distinguishing graphite from the diamond or amorphous charcoal, Berthelot showed that when compounds of carbon and hydrogen are decomposed by heat, amorphous charcoal is mainly formed, whilst when compounds of carbon with chlorine, sulphur, and boron are decomposed, graphite is principally deposited.

^{15a} Diamonds are found in a particular dense rock, known by the name of itacolumnite, and are dug out of the *débris* produced by the destruction of the itacolumnite by water; when the *débris* is washed the diamonds remain behind. They are found principally in Brazil, in the provinces of Rio and Bahia, and at the Cape of Good Hope. The *débris* gives the black or amorphous diamond, carbonado, and the ordinary colourless or yellow translucent diamond. As the diamond possesses a very marked cleavage, the first operation consists in splitting it, and then roughly and finely polishing it with diamond powder. It is very remarkable that Professors P. A. Latchinoff and Eroféeff found (1887) diamond powder in a meteoric stone which fell in the Government of Penza, in the district of Krasnoslobodsk, near the settlement of Novo Urei (Sept. 10, 1886). Up to that time charcoal and graphite (a special variety, cliftonite) had been found in meteorites and the diamond only conjectured to occur therein. The Novo Urei meteorite was composed, like many others, of siliceous matter and metallic iron (with nickel). Rossel (1896) found minute particles of diamond in hardened steel.

¹⁶ Diamonds are sometimes found in the shape of small balls, and in that case it is impossible to cut them because directly the surface is ground or broken they fall into minute pieces. Sometimes minute diamond crystals form a dense mass like sugar, and this is generally reduced to diamond powder and used for grinding. Some known varieties of the diamond are almost opaque and of a black colour. Such diamonds are as hard as the ordinary ones, and are used for polishing diamonds and other precious stones, and also for rock boring and tunnelling. They evolve gas, and become almost or quite colourless when heated to 200°.

electrode, when a weak galvanic current is passed through liquid chloride of carbon.^{16a}

Moissan (Paris, 1893) produced artificial diamonds at the high temperature attained in the electric furnace¹⁷ by dissolving carbon in molten cast iron, and allowing the solution or alloy containing CFe_3 to cool under the powerful pressure exerted by rapidly cooling the metal.^{17a}

^{16a} Hannay, in 1880, obtained diamonds by heating a mixture of heavy liquid hydrocarbons (paraffin oils) with magnesium in a thick iron tube. This investigation, however, was not repeated.

¹⁷ The **electric furnace** is an invention of recent times, and gives the possibility of obtaining a temperature of 3500° , which is unattainable not only in ordinary furnaces, but even in the oxyhydrogen flame, the temperature of which does not exceed 2000° . The electric furnace consists of two pieces of lime, laid one on the other. A cavity is made in the lower piece for the reception of the substance to be melted between two thick electrodes of dense carbon. On passing a current of 70 volts and 450 ampères a temperature of 3000° is easily obtained. At a temperature of 2500° (100 ampères and 40 volts) not only do all metals melt, but even lime and magnesia (when placed in the space between the carbon electrodes, i.e. in the voltaic arc) become soft and crystallise on cooling. At 3000° lime becomes very fluid, and volatilises and yields metallic calcium, which partially separates out, and a carbon compound, which remains liquid for a long time. At this temperature oxide of uranium is reduced to the suboxide and metal, zirconia and rock crystal fuse and partially volatilise, as also does alumina; platinum, gold, and even carbon appreciably volatilise; the majority of the metals form carbides. Moissan gives the following interesting example to show the effect of the different temperatures obtained in the electric furnace. A current of 100 ampères and 50 volts reduces titanous anhydride to the lower oxide. With 300 ampères and 70 volts a molten yellow nitride of titanium is formed; whilst with 1200 ampères and 70 volts carbide of titanium is formed—that is, the carbon replaces the nitrogen which is evolved owing to the rise of temperature. Most of Moissan's experiments with the electric furnace were made in the years 1892–1899.

^{17a} Moissan first investigated the solution of carbon in molten metals (and the formation of the carbides) such as magnesium, aluminium, iron, manganese, chromium, uranium, silver, platinum, and silicon. At the same time Friedel, owing to the discovery of the diamond in meteoric iron, admitted that the formation of the diamond is dependent upon the influence of iron and sulphur. With this object, that is, in order to obtain the diamond, Friedel caused sulphur to react upon samples of cast iron rich in carbon, in a closed vessel at a maximum temperature of 500° , and after dissolving the sulphide of iron formed, he obtained a small quantity of a black powder which scratched corundum, i.e., diamond. Moissan's experiments (1893) were more successful, probably owing to his employment of the electric furnace. If iron is saturated with carbon at a temperature between 1100° and 3000° , then at 1100° – 1200° a mixture of amorphous carbon and graphite is formed, while at 3000° graphite alone is obtained in very beautiful crystals. Thus, under these conditions the diamond is not formed, and it can only be obtained if the high temperature be aided by powerful pressures. For this purpose Moissan took advantage of the pressure produced in the passage of a mass of molten carbide of iron, Fe_3C , in passing from the liquid to the solid state, as it increases in volume on solidifying, and when thrown into water forms a crust, which compresses the internal mass in which a portion of the carbon separates out in the form of the diamond. He first melted 150–200 grams of iron in the electric furnace, and quickly introduced a cylinder of carbon into the molten iron. He then removed the crucible with the molten iron from the furnace and plunged it into a reservoir containing water. After treatment with boiling hydrochloric acid, three varieties of carbon were obtained (if the crust remained

Judging from the fact that carbon forms a number of gaseous bodies (carbonic oxide, carbonic anhydride, methane, ethylene, acetylene, &c.) and volatile substances (for example, many hydrocarbons and their most simple derivatives), and considering that the atomic weight of carbon, 12, approaches that of nitrogen, 14, and that of oxygen, 16, and that the compounds CO (carbonic oxide) and N₂C₂ (cyanogen) are gases, it may be argued that if carbon formed the molecule C₂, like N₂ and O₂, it would be a gas. And as by polymerisation or the combination of like molecules (the passage of O₂ into O₃ or of NO₂ into N₂O₄), the temperatures of ebullition and fusion rise (which is particularly clearly proved with the hydrocarbons of the C_nH_{2n} series), we must assume that **the molecules of charcoal, graphite, and the diamond are very complex**, seeing that they are substances far removed from a gaseous state. The aptitude which the atoms of carbon show for combining together and forming complex molecules appears in all carbon compounds. Among the volatile compounds of carbon many are well known, the molecules of which contain C₅ . . . C₁₀ . . . C₂₀ . . . C₃₀, &c., in general C_n, where *n* may be very large, and in none of the other elements is this faculty of complexity so greatly developed as in carbon.¹⁸ Up to the present time there is no basis for determining the degree of polymerisation of the charcoal, graphite, or diamond molecules, and it can only be supposed that they contain C_n, where *n* is a large quantity. Charcoal and those complex non-volatile organic substances which represent the gradual transitions

intact; otherwise it would only contain Fe₂C and graphite): (1) a small amount of graphite (if the cooling be rapid); (2) carbon of a chestnut colour in very fine twisted threads, showing that it had been subjected to a very high pressure (a similar variety was met with in various specimens of the Canon Diablo meteorites); and lastly (3) an inconsiderable quantity of an exceeding dense mass which was freed from the admixture of the lighter modifications by treatment with *aqua regia*, sulphuric and hydrofluoric acids, and from which Moissan, by means of liquid bromoform (sp. gr. 2.900), succeeded in separating some small pieces, having a greater density than bromoform, which scratched the ruby and had the properties of the diamond. Some of these pieces were black, others were transparent and refracted light strongly. The dark grey tint of the former resembled that of the black diamonds (carbonado). Their density was between 3 and 3.5. K. Chrustchoff showed that at its boiling-point silver dissolves 6 per cent. of carbon. This silver was rapidly cooled, so that a crust formed on the surface and prevented the metal expanding, and thus produced a powerful pressure. A portion of the carbon which separates out under these conditions exhibits the properties of the diamond. Rousseau, for the same purpose, heated carbide of calcium in the electric furnace. There is no doubt that all these investigators obtained the diamond as a transparent body, which burnt into CO₂, and possessed an exceptional hardness, but only in the form of a fine powder.

¹⁸ The existence (up to 600°) of molecules S₈ and S₆ is known, and it must be held that this accounts for the formation of hydrogen persulphide, H₂S₂. Phosphorus appears in the molecule P₄ and gives P₄H₂. When expounding the data on specific heat we shall have occasion to return to the question of the complexity of the carbon molecule.

to charcoal¹⁹ and form the principal solid substances of organisms, contain a store or accumulation of internal power in the form of the energy binding the atoms into complex molecules. When charcoal or complex compounds of carbon burn, the energy of the carbon and oxygen is turned into heat, and this fact is taken advantage of at every turn for the generation of heat from fuel.²⁰

No other two elements are capable of combining together in such variety as carbon and hydrogen. The **hydrocarbons** of the C_nH_{2m} series in many cases differ widely from each other, although they have some properties in common. All hydrocarbons, whether gaseous, liquid, or solid, are combustible substances sparingly soluble or insoluble in water. The liquefied gaseous hydrocarbons, as well as those which are liquid at ordinary temperatures, and those solid hydrocarbons which have been liquefied by fusion, have the appearance and property of oily liquids, more or less viscous or fluid.²¹ The solid

¹⁹ The hydrocarbons poor in hydrogen and containing many atoms of carbon, like chrysene and carbopetrocene, &c., $C_nH_{2(n-m)}$, are solids, and become less fusible as n and m increase. They present a certain approach to the properties of the diamond. And in proportion to the diminution of the water in the carbohydrates $C_nH_{2m}O_m$ —for example in the humic compounds (note 5)—the transition of complex organic substances to charcoal is very evident. That residue resembling charcoal and graphite which is obtained by the separation (by means of copper sulphate and sodium chloride) of iron from white cast iron containing carbon chemically combined with the iron, also seems, especially after the researches of G. A. Zaboudsky, to be a complex substance containing $C_{12}H_6O_3$. The endeavours which have been directed towards determining the measure of complexity of the molecules of charcoal, graphite, and the diamond, will probably at some period lead to the solution of this problem and will most likely prove that the various forms of charcoal, graphite, and the diamond contain molecules of different and very considerable complexity. The constancy of the grouping of benzene, C_6H_6 , and the wide diffusion and facility of formation of the carbohydrates containing C_6 (for example, cellulose, $C_6H_{10}O_5$, glucose, $C_6H_{12}O_6$) give reason for thinking that the group C_6 is the first and simplest of those possible to free carbon, and it may be hoped that some time or other it may be possible to get carbon in this form. Perhaps in the diamond there may be found such a relation between the atoms as exists in the benzene group, and in charcoal such as is found in carbohydrates.

²⁰ When charcoal burns, the complex molecule C_n is resolved into the simple molecules nCO_2 , and therefore part of the heat—probably no small amount—is expended in the destruction of the complex molecule C_n . Perhaps by burning the most complex substances, which are the poorest as regards hydrogen, it may be possible to form an idea of the work required to split up C_n into separate atoms.

²¹ The **viscosity**, or degree of mobility, of **liquids** is determined by their *internal friction*. It is estimated by passing the liquids through narrow (capillary) tubes, the mobile liquids passing through with greater facility and speed than the viscous ones. The viscosity varies with the temperature and nature of the liquids, and in the case of solutions changes with the amount of the substance dissolved, but is not proportional to it. So that, for example, with alcohol at 20° the viscosity will be 69, and for a 50 per cent. solution 160, the viscosity of water being taken as 100. The volume of the liquid which passes through is, both by experiment (Poiseuille) and by theory (Stokes), proportional to the time, the pressure, and the fourth power of the diameter of the (capillary) tube, and inversely proportional to the length of the tube; this renders it

hydrocarbons more or less resemble wax in their properties, although ordinary oils generally contain oxygen and wax in addition to carbon and hydrogen, but in relatively small proportion. There are also many hydrocarbons which have the appearance of tar—as, for instance, metacinnamene and gutta-percha. Those liquid hydrocarbons which boil at a high temperature are like oils, and those which have a low boiling-point resemble ether, whilst the gaseous hydrocarbons in many of their properties are akin to hydrogen. All this tends to show that in hydrocarbons physically considered the properties of solid non-volatile charcoal are strongly modified and hidden, whilst those of the hydrogen predominate. All hydrocarbons are neutral substances (neither basic nor acid), but under certain conditions they enter into peculiar reactions. It has been seen in those hydrogen compounds which have been already considered (water, nitric acid, ammonia) that in almost all cases the hydrogen enters into reaction, being displaced by metals. The hydrogen of the hydrocarbons, it may be said, has no metallic character—that is to say, it is not directly²² displaced by metals, even such as sodium and potassium. On the application of more or less heat all hydrocarbons decompose,²³ forming charcoal and hydrogen. The majority of the hydrocarbons do not combine with

possible to form comparative estimates of the coefficients of internal friction and viscosity.

As the complexity of the molecules of hydrocarbons and their derivatives increases by the addition of carbon (or CH_2), so also does the degree of viscosity. The extensive series of investigations referring to this subject belong to the province of physical chemistry. That connection which (already partly observed) ought to exist between the viscosity and the other physical and chemical properties obliges us to conclude that the magnitude of the internal friction plays an important part in molecular mechanics. It has already been seen from existing data that at the absolute boiling-point the viscosity becomes as small as it is in gases.

²² In a number of hydrocarbons and their derivatives such a substitution of metals for the hydrogen may be attained by indirect means. The property shown by acetylene, C_2H_2 , and its analogues, of forming metallic derivatives is in this respect particularly characteristic. Judging from the fact that carbon is an acid element (that is, gives an acid anhydride with oxygen), though only comparatively slightly so (for carbonic acid is not at all a strong acid and compounds of chlorine and carbon, even CCl_4 , are not decomposed by water, as is the case with phosphorus chloride and even silicic chloride and boric chloride, although these correspond with acids of but little energy), one might expect to find in the hydrogen of hydrocarbons this faculty for being substituted by metals. The metallic compounds which correspond with hydrocarbons are known under the name of *organo-metallic compounds* if they contain both a metal and hydrogen. Such, for instance, is zinc ethyl, $\text{Zn}(\text{C}_2\text{H}_5)_2$, which corresponds with ethyl hydride or ethane, C_2H_6 , two atoms of hydrogen in the latter having been exchanged for one of zinc. The compounds of carbon with a metal only are called *carbides*, for instance, carbide of calcium, C_2Ca (Chap. XIV.).

²³ Gaseous and volatile hydrocarbons decompose when passed through a heated tube or introduced into the voltaic arc. When hydrocarbons are decomposed by heating, the primary products are generally other more stable hydrocarbons, among which are acetylene, C_2H_2 , benzene, C_6H_6 , naphthalene, C_{10}H_8 , &c.

the oxygen of the air or oxidise at ordinary temperatures, but under the action of nitric acid and many other oxidising substances most of them undergo oxidation, in which either a portion of the hydrogen and carbon is separated, or the oxygen enters into combination.²⁴ When heated in air, hydrocarbons burn, and, according to the amount of carbon they contain, their combustion is attended with a separation of more or less soot—that is, finely divided charcoal—which imparts great brilliancy to the flame, and on this account many of them are used for the purposes of illumination—as, for instance, kerosene, coal gas, oil of turpentine, and acetylene. As hydrocarbons contain reducing elements (that is, those capable of combining with oxygen), they often act as reducing agents—for instance, when heated with oxide of copper, they burn, forming carbonic anhydride and water, and leave metallic copper. Gerhardt proved that all hydrocarbons contain an **even number of hydrogen atoms**. Therefore the general formula for all hydrocarbons is C_nH_{2m} , where n and m are whole numbers. This fact is known as **the law of even numbers** (the cause of which is explained in the following pages as a consequence of the laws of substitution and of limits). Hence, the simplest possible hydrocarbons ought to be: CH_2 , CH_4 , CH_6 . . . C_2H_2 , C_2H_4 , C_2H_6 , C_2H_8 . . . but they do not all exist, since the quantity of H which can combine with a certain amount of carbon is limited, as we shall learn directly.

Some of the hydrocarbons are capable of combination, whilst others do not show that power. Those which contain less hydrogen belong to the former category, and those which, for a given quantity of carbon, contain the maximum amount of hydrogen belong to the latter. The composition of those last mentioned is expressed by the general formula C_nH_{2n+2} . These so-called **saturated hydrocarbons** are incapable of combination.²⁵ The hydrocarbons CH_4 , C_2H_6 , C_3H_8 , &c. . . . do not

²⁴ E. E. Wagner (1888) showed that when certain unsaturated hydrocarbons are shaken with a weak (1 per cent.) solution of potassium permanganate, $KMnO_4$, at ordinary temperatures, they form glycols—for example, C_2H_4 yields $C_2H_6O_2$, i.e., both water and oxygen are taken into combination.

²⁵ My article on this subject appeared in the *Journal of the St. Petersburg Academy of Sciences* in 1861. Up to that time, although many additive combinations with hydrocarbons and their derivatives were known, they had not been generalised, and were even continually being quoted as cases of substitution. Thus the combination of ethylene, C_2H_4 , with chlorine, Cl_2 , was often regarded as a formation of the products of the substitution of C_2H_3Cl and HCl , which it was supposed were held together as is the water of crystallisation in salts. Even earlier than this (1857, *Journal of the Petroffsky Academy*) I considered similar cases as true compounds. In general, according to the law of limits, an unsaturated hydrocarbon, or its derivative, on combining with any compound, gives a substance which is either saturated or else approaching the limit. The investigations of Frankland with many organo-metallic compounds clearly showed the limit in the case of metallic compounds, which we shall constantly refer to later on; but carbon also has its limit, attained in C_nH_{2n+2} .

exist. Those containing the maximum amount of hydrogen will be represented by CH_4 ($n = 1$, $2n + 2 = 4$), C_2H_6 ($n = 2$), C_3H_8 ($n = 3$), C_4H_{10} , &c. This may be termed **the law of limits**. Placing this in juxtaposition with the law of even numbers, it is easy to perceive that the possible hydrocarbons can be ranged in series, the terms of which may be expressed by the general formulæ $\text{C}_n\text{H}_{2n+2}$, C_nH_{2n} , $\text{C}_n\text{H}_{2n-2}$, &c. . . . Those hydrocarbons which contain for n atoms of carbon a number of atoms of hydrogen expressed in terms of n are said to be *homologous* with one another. Thus, the hydrocarbons CH_4 , C_2H_6 , C_3H_8 , C_4H_{10} , &c. . . . are members of the limiting (saturated) homologous series $\text{C}_n\text{H}_{2n+2}$. So that the difference between any two members of an homologous series is $n\text{CH}_2$.²⁶ Not only the composition but also the properties of the members of a series tend to classification in one group. For instance, the members of the series $\text{C}_n\text{H}_{2n+2}$ are not capable of forming additive compounds, whilst those of the series C_nH_{2n} are capable of combining with chlorine, sulphuric anhydride, &c.; and the members of the $\text{C}_n\text{H}_{2n-6}$ group, belonging to the coal tar series, are easily nitrated (give nitro-compounds, Chapter VI.), and have other properties in common. The physical properties of the members of a given homologous series vary in some such manner as this; the boiling-point generally rises and the internal friction increases as n becomes greater²⁷—that is, as the relative amount of carbon and the molecular weight increase; the specific gravity also changes regularly as n becomes greater.²⁸

²⁶ The conception of homology has been applied by Gerhardt to all organic compounds in his classical work, *Traité de Chimie Organique*, finished in 1855 (4 vols.), in which he divided all organic compounds into *fatty* and *aromatic*, a classification which is in principle still adhered to, although the latter are more often called benzene derivatives, on account of the fact that Kekulé, in his beautiful investigations on the structure of aromatic compounds, showed the presence in them all of the 'benzene ring or nucleus,' C_6H_6 .

²⁷ This is always true for hydrocarbons, but for derivatives of the lower homologues the law is sometimes different; for instance, in the series of saturated alcohols, $\text{C}_n\text{H}_{2n+1}(\text{OH})$, when $n=0$, we obtain water, $\text{H}(\text{OH})$, which boils at 100° , and whose specific gravity at 15° is 0.9992; when $n=1$, we have wood spirit, $\text{CH}_3(\text{OH})$, which boils at 66° , and at 15° has a specific gravity, 0.7964; $n=2$ gives ordinary alcohol, $\text{C}_2\text{H}_5(\text{OH})$, boiling at 78° and having the specific gravity 0.7936 at 15° ; with further increase of CH_2 the specific gravity increases. For the glycols, $\text{C}_n\text{H}_{2n}(\text{OH})_2$, the phenomenon of a similar kind is still more striking; at first the temperature of the boiling-point and the density increase, and then for higher (more complex) members of the series diminish. The reason for this, it is evident, must be sought for in the influence and properties of water, and that strong affinity which, acting between hydrogen and oxygen, determines many of the exceptional properties of water (Chapter I.)

²⁸ As, for example, in the saturated series of hydrocarbons, $\text{C}_n\text{H}_{2n+2}$, the lowest member ($n=0$) must be taken as hydrogen H_2 , a gas which (with a critical temperature below -190°) is liquefied with great difficulty, and when in a liquid state has doubtless a very small density. Where $n=1, 2, 3$, we have the hydrocarbons CH_4 , C_2H_6 , C_3H_8 ,

Many of the hydrocarbons met with in nature are the products of organisms, and do not belong to the mineral kingdom. A still greater number are produced artificially. These are formed by what is termed the combination of residues. For instance, if a mixture of the vapours of hydrogen sulphide and carbon bisulphide be passed through a tube in which copper is heated, the latter absorbs the sulphur from both the compounds, and the liberated carbon and hydrogen combine to form a hydrocarbon, methane. If carbon be combined with any metal and this compound MC_n be treated with an acid, HX , then the haloid X will give a salt with the metal and the residual carbon and hydrogen will yield a hydrocarbon. Thus cast iron, which contains a compound of iron and carbon, gives liquid hydrocarbons like naphtha under the action of acids. C_2Ca gives acetylene C_2H_2 . If a mixture of bromo-benzene, C_6H_5Br , and ethyl bromide, C_2H_5Br , be heated with metallic sodium, the sodium combines with the bromine of both compounds, forming sodium bromide, $NaBr$, and the residues combine together, giving the compound $C_6H_5.C_2H_5$ or C_8H_{10} . Hydrocarbons are also produced by the breaking up of more complex organic or hydrocarbon compounds, especially by heating—that is, by dry distillation. For instance, gum-benzoin contains an acid called benzoic acid, $C_7H_6O_2$, the vapours of which, when passed through a heated tube, split up into carbonic anhydride, CO_2 , and benzene, C_6H_6 . Carbon and hydrogen only unite directly in one ratio of combination—namely, to form acetylene, having the composition C_2H_2 , which, as compared with other hydrocarbons, exhibits very great stability at a high temperature.²⁹

which are gases, more and more readily liquefiable. The absolute boiling-point for CH_4 is -100° , and for ethane, C_2H_6 , and the higher members it rises. The hydrocarbon C_4H_{10} liquefies at about 0° . C_5H_{12} in some of its isomeric forms boils at from $+9^\circ$ (Lvoff) to 37° , C_6H_{14} from 58° to 78° , &c. The specific gravities in a liquid state at 15° increase appreciably with n :

C_5H_{12}	C_6H_{14}	C_7H_{16}	$C_{10}H_{22}$	$C_{16}H_{34}$
0.63	0.66	0.70	0.75	0.85

²⁹ If at the ordinary temperature (assuming therefore that the water formed will be in a liquid state) a gram molecule (26 grams) of acetylene, C_2H_2 , be burnt, 310 thousand calories will be emitted (Thomsen), and as 12 grams of charcoal produce 97 thousand calories, and 2 grams of hydrogen 69 thousand calories, it follows that, if the hydrogen and carbon of the acetylene were burnt there would be only $2 \times 97 + 69$, or 263 thousand calories produced. It is evident, then, that acetylene in its formation from carbon and hydrogen *absorbs* 310–263, or 47 thousand calories. The reason of this must first be sought in the fact that the solid carbon has passed into a gas, and, as it were, disseminated throughout the hydrogen. In the formation of CH_4 , C_2H_6 , &c., however, a contraction has taken place with regard to the hydrogen, which should be accompanied by the evolution of heat. In this way the thermo-chemical data represent the result of the sum of the physical and chemical changes accomplished.

As regards the combustion of carbon compounds, we will first enumerate the

There is one substance known among the hydrocarbons composed of 1 atom of carbon and 4 atoms of hydrogen ; this is the compound containing the highest percentage of hydrogen (CH_4 contains 25 per cent. of hydrogen), and at the same time it is the only hydrocarbon whose molecule contains but a single atom of carbon. This saturated hydrocarbon, CH_4 , is called **marsh gas** or **methane**. If vegetable or animal refuse suffers decomposition in a space to which air has not free access, or no access at all, then the decomposition is accompanied with the formation of marsh gas, and this either at the ordinary temperature or at a comparatively much higher one. On this account **plants**, when decomposing under water in **marshes**, give out this gas.^{29a} It is well known that if the mud in bogs be stirred up, the act is accompanied with the evolution of a large quantity of gas bubbles ; these may, although slowly, also separate of their own accord. The gas which is

quantities of heat separated by the combustion of definite chemical carbon compounds, and then give a few figures bearing on the kinds of fuel used in practice.

For molecular quantities the following amounts of **heat** are given out in complete **combustion** (when gaseous carbonic anhydride and liquid water are formed), according to Thomsen's data : (1) for gaseous $\text{C}_n\text{H}_{2n+2}$: $52.8 + 158.8n$ thousand calories ; (2) for C_nH_{2n} : $17.7 + 158.1n$ thousand calories ; (3) according to Stohmann (1888), for liquid saturated alcohols, $\text{C}_n\text{H}_{2n+2}\text{O}$: $11.8 + 156.3n$, and as the latent heat of evaporation is about $8.2 + 0.6n$, in the gaseous state, the value will be $20.0 + 156.9n$; (4) for monobasic saturated liquid acids, $\text{C}_n\text{H}_{2n}\text{O}_2$: $95.3 + 154.3n$, and (as their latent heat of evaporation is about $5.0 + 1.2n$) in a gaseous form, about $90 + 155n$; (5) for solid saturated bibasic acids, $\text{C}_n\text{H}_{2n-2}\text{O}_4$: $253.8 + 152.6n$, or, if they are expressed as $\text{C}_n\text{H}_{2n}\text{C}_2\text{H}_2\text{O}_4$, $51.4 + 152.6n$; (6) for benzene and its liquid homologues (still according to Stohmann) $\text{C}_n\text{H}_{2n-6}$: $158.6 + 156.3n$, and in the gaseous state about $155 + 157n$; (7) for the gaseous homologues of acetylene, $\text{C}_n\text{H}_{2n-2}$ (according to Thomsen), $5 + 157n$. It is evident from the preceding figures that the group CH_2 , or CH_3 substituted for H, on burning, gives out from 152 to 159 thousand calories. This is less than that given out by $\text{C} + \text{H}_2$, which is $97 + 69$ or 166 thousand. According to Stohmann, for dextro-glucose, $\text{C}_6\text{H}_{12}\text{O}_6$, the heat of combustion is 65 ; for common sugar, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, 1322 ; for cellulose, $\text{C}_6\text{H}_{10}\text{O}_5$, 672 ; starch, 662 ; dextrin, 666.2 ; glycol, $\text{C}_2\text{H}_6\text{O}_2$, 281.7 ; glycerine, 397.2, &c. The heats of combustion of the following solids (determined by Stohmann) are expressed per unit of weight : naphthalene, C_{10}H_8 , 9,621 ; urea, $\text{CN}_2\text{H}_4\text{O}$, 2,465 ; white of egg, 5,579 ; dry rye bread, 4,421 ; wheaten bread, 4,302 ; tallow, 9,365 ; butter, 9,192 ; linseed oil, 9,323. A collection of arithmetical data for the heats of combustion will be found in V. F. Longinin's work, *Description of the various Methods of Determining the Heats of Combustion of Organic Compounds* (Moscow, 1894).

The number of units of heat given out by *unit weight* during the complete combustion and cooling of the ordinary kinds of **fuel** in their usual state of dryness and purity may be taken as $Q = 81c + 300h - 26(o - s)$, where c , h , o , and s express the percentage amounts of carbon, hydrogen, oxygen, and sulphur respectively in the fuel. For instance, for naphtha containing 86 per cent. carbon, 12 of hydrogen, and 2 of oxygen, Q is found by experiment and calculation to be about 10,500 calories. The above formula is given in my work on fuel (see note 1). The same work shows also that 890 to 935 calories are yielded for every cubic metre of air in the combustion of all kinds of solid fuel, if the water remains in the products of combustion in the form of vapour. Gaseous fuels give as much as 1,000 calories per cubic metre of air.

^{29a} Manure, decomposing under the action of bacteria, evolves CO and CH_4 .

evolved consists principally of marsh gas.³⁰ When wood, coal, and many other vegetable and animal substances are decomposed by the **action of heat** without access of air—that is, are subjected to dry distillation—they evolve in addition to many other gaseous products of decomposition (carbonic anhydride, hydrogen, and various other substances), a great deal of methane. Generally the gas which is used for lighting purposes is obtained by this means, and therefore always contains marsh gas, mixed with dry hydrogen and other vapours and gases, although it is subsequently purified from many of them.³¹ As the

³⁰ It is easy to collect the gas which is evolved in marshy places if a glass bottle be inverted in the water and a funnel put into it (both being filled with water); if the mud of the bottom be now agitated, the bubbles which rise may be easily caught by the inverted funnel.

³¹ **Illuminating gas** is generally prepared by heating gas coal rich in bitumen in oval cylindrical horizontal cast-iron or clay retorts. Several such retorts *BB* (fig. 58) are disposed in the furnace *A*, and heated together. When the retorts are heated to a red heat, lumps of coal are thrown into them, and they are then closed with a tightly fitting cover. The illustration shows the furnace, with five retorts. Coke (see note 1, dry distillation) remains in the retorts, and the volatile products in the form of vapours and gases travel along the pipes *d*, rising from each retort. These pipes branch above the stove, and communicate with the receiver *f* (hydraulic main) placed above the furnace. Those products of the dry distillation which most easily pass from the gaseous into the liquid and solid states collect in the hydraulic main. From the latter the vapours and gases travel along the pipe *g* and the series of vertical pipes *j* (which are sometimes cooled by water trickling over the surface), in which the vapours and gases cool owing to contact with the colder surface, and a fresh quantity of vapour condenses. The condensed liquids pass from the pipes *g* and *j* and into the troughs *H*. These troughs always contain liquid at a constant level (the excess flowing away) so that the gas cannot escape, and thus they form, as it is termed, a hydraulic joint. In the state in which it leaves the condensers the gas consists principally of the following vapours and gases: (1) vapour of water, (2) ammonium carbonate, (3) liquid hydrocarbons, (4) hydrogen sulphide, H_2S , (5) carbonic anhydride, CO_2 , (6) carbonic oxide, CO , and (7) sulphurous anhydride, SO_2 ; but a great part of the illuminating gas consists of (8) hydrogen, (9) marsh gas, (10) olefiant gas, C_2H_4 , and other gaseous hydrocarbons. The hydrocarbons (3, 9, and 10), the hydrogen, and carbonic oxide are capable of combustion, and are useful constituents, but the carbonic anhydride, the hydrogen sulphide, and sulphurous anhydride, as well as the vapours of ammonium carbonate, form an injurious admixture, because they do not burn (CO_2 , SO_2) and lower the temperature and brilliancy of the flame, or else, although capable of burning (for example, H_2S , CS_2 , and others), they give out during combustion sulphurous anhydride which has a disagreeable smell, is injurious when inhaled, and spoils many surrounding objects. In order to separate the injurious products, the gas is washed with water, a cylinder (not shown in the illustration) filled with coke continually moistened with water serving for this purpose. The water coming into contact with the gas dissolves the ammonium carbonate; hydrogen sulphide, carbonic anhydride, and sulphurous anhydride, being only partly soluble in water, have to be got rid of by special means. To this end the gas is passed through moist lime or other alkaline liquid, as the above-mentioned gases have acid properties and are therefore retained by the alkali. When lime is used, calcium carbonate, sulphite and sulphide, all solid substances, are formed. It is necessary to renew the purifying material as its absorbing power decreases. A mixture of lime and sulphate of iron, FeSO_4 , acts still better, because the latter, with lime, $\text{Ca}(\text{HO})_2$, forms ferrous hydroxide, $\text{Fe}(\text{HO})_2$ and gypsum, CaSO_4 . The suboxide (partly turning into oxide) of iron absorbs

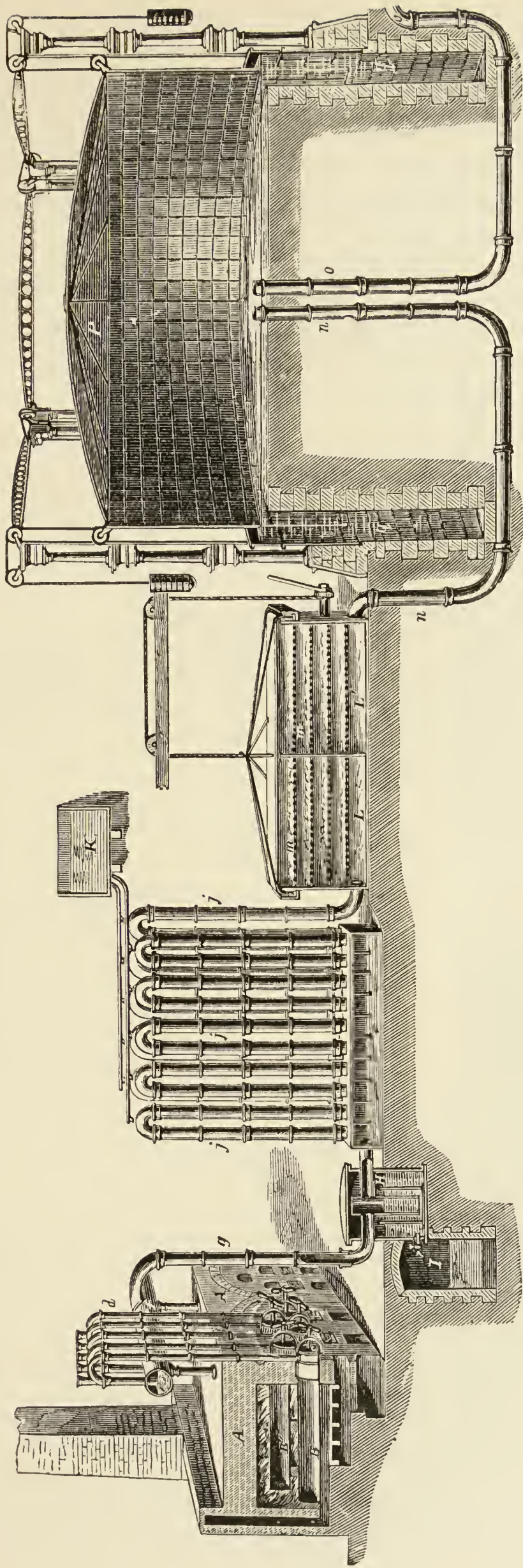


FIG. 66.—General view of gas works, *B*, retorts; *f*, hydraulic main; *H* and *I*, tar well; *i*, condensers; *L*, purifiers; *P*, gasholder.

decomposition of the organic matter, which forms coal, is still going on underground, the evolution of large quantities of marsh gas frequently

H_2S , forming FeS and H_2O , and the gypsum retains the remainder of the ammonia, the excess of lime absorbing carbonic anhydride and sulphuric anhydride. [In English works a native hydrated ferric hydroxide is used for removing hydrogen sulphide.] This purification of the gas takes place in the apparatus *L*, where the gas passes through perforated trays *m*, covered with sawdust mixed with lime and sulphate of iron. It is necessary to remark that in the manufacture of gas it is indispensable to draw off the vapours from the retorts, so that they should not remain there long (otherwise the hydrocarbons would in a considerable degree be resolved into carbon and hydrogen),

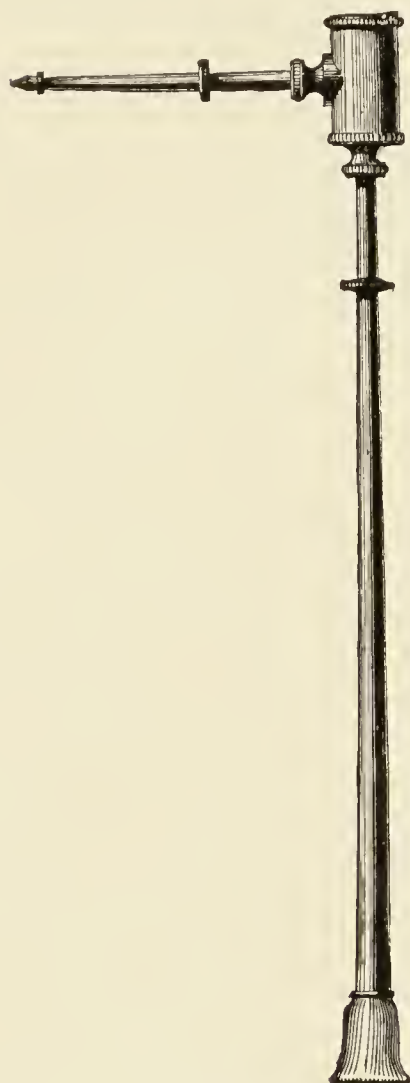


FIG. 67. — Blowpipe. Air is blown in at the trumpet-shaped mouthpiece, and escapes in a fine stream from the platinum jet placed at the extremity of the side tube.

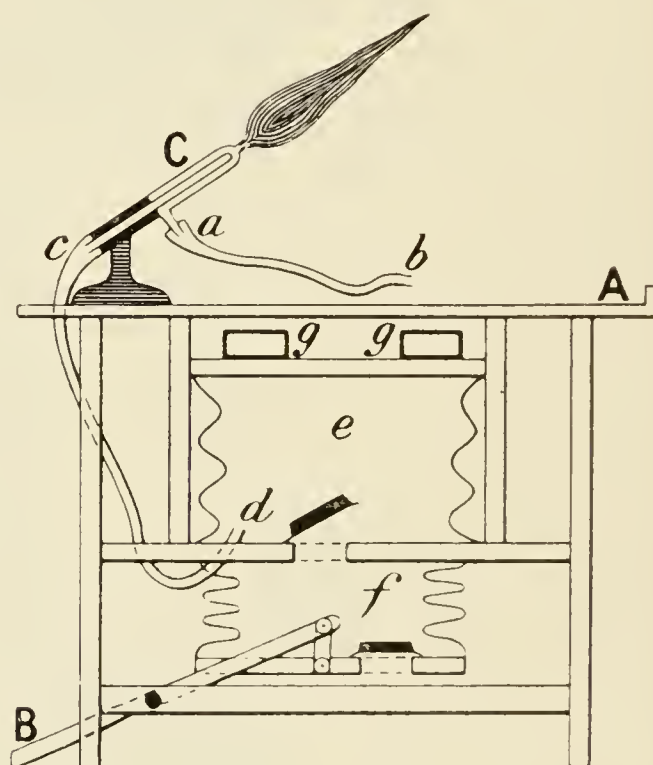


FIG. 68. — Blowpipe table A B with gas blowpipe C, into which the gas passes by the tube *a b* and the air by the tube *c d* connected with the bellows *e f*, which are worked by means of the lever B and the weights *g*.

and also to avoid a great pressure of gas in the apparatus, otherwise a quantity of gas would escape at all cracks such as must inevitably exist in such a complicated arrangement. For this purpose there are special pumps (exhausters) so regulated that they only pump off the quantity of gas formed (the pump is not shown in the illustration). The purified gas passes through the pipe *n* into the *gasometer* (gasholder) *P*, which is a dome made of iron plate. The edges of the dome dip into water poured into a ring-shaped channel, *g*, in which the sides of the dome rise and fall. The gas is collected in this holder, and distributed to its destination by pipes communicating with the pipe *o*, issuing from the dome. The pressure of the holder on the gas enables it, on issuing from a long pipe, to pass through the small aperture of the burner. A hundred kilograms of coal give about 20 to 30 cubic metres of gas, having a density from four to nine times greater than that of hydrogen. A cubic metre (1,000 litres) of hydrogen

occurs in coal mines.³² When mixed with air it gives an explosive mixture, which forms one of the great dangers of coal mining, as subterranean work has always to be carried on by lamp-light. This danger is, however, overcome by the use of *Humphry Davy's safety-lamp*.³³

weighs about 87 grams; therefore 100 kilograms of coal give about 18 kilograms or about one-sixth of its weight of gas. Illuminating gas is generally lighter than marsh gas, as it contains a considerable amount of hydrogen, and is only heavier than marsh gas when it contains much of the heavier hydrocarbons. Thus olefiant gas, C_2H_4 , is fourteen times, and the vapours of benzene thirty-nine times, heavier than hydrogen, and illuminating gas sometimes contains 15 per cent. of its volume of them. The brilliancy of the flame of the gas increases with the quantity of olefiant gas and similar heavy hydrocarbons, as it then contains more carbon for a given volume, and a greater number of carbon particles are separated. Gas usually contains from 35 to 60 per cent. of its volume of marsh gas, from 30 to 50 per cent. of hydrogen, from 3 to 5 per cent. of carbonic oxide, from 2 to 10 per cent. of heavy hydrocarbons, and from 3 to 10 per cent. of nitrogen. Wood gives almost the same sort of gas as coal and in about the same quantity; but the wood gas contains a great deal of carbonic anhydride, although on the other hand there is an almost complete absence of sulphur compounds. Tar, oils, naphtha, and similar materials furnish a large quantity of good illuminating gas. An ordinary burner of 8 to 12 candle-power burns 5 to 6 cubic feet of coal gas per hour, but only a cubic foot of naphtha gas. One pood (36 lb. Eng.) of naphtha gives 500 cubic feet of gas—that is, one kilogram of naphtha produces about one cubic metre of gas. The formation of combustible gas on heating coal was discovered in the beginning of the eighteenth century, but was only put into practice towards the end of it by Le-Bon in France and Murdoch in England. In England, Murdoch, together with the renowned Watt, built the first gas works in 1805.

In practice illuminating gas is used not only for lighting (electricity and kerosene are cheaper in Russia), but also as the motive power for gas engines (see p. 175), which consume about half a cubic metre per horse-power per hour; gas is also used in laboratories for heating purposes. When it is necessary to concentrate the heat, either the ordinary blowpipe (fig. 67) is applied, placing the end in the flame and blowing through the mouthpiece; or, in other forms, gas is passed through the blowpipe; when a large, hot, smokeless flame is required for heating crucibles or glass-blowing, a foot-blower is used. High temperatures, which are often required for laboratory and manufacturing purposes, are most easily attained by the use of gaseous fuel (illuminating gas, producer gas, and water gas, which will be treated of in the following chapter), because complete combustion may be effected without access of air. It is evident that in order to obtain high temperatures means must be taken to diminish the loss of heat by radiation, and to ensure perfect combustion.

³² The gas which is set free in coal mines contains nitrogen, some carbonic anhydride, and a large quantity of marsh gas. The best means of avoiding an explosion consists in efficient ventilation. It is best to light coal mines with electric lamps.

³³ The Davy lamp, of which an improved form is represented in the accompanying figure, is used for lighting coal mines and other places where combustible gas is found. The wick of the lamp is enclosed in a thick glass

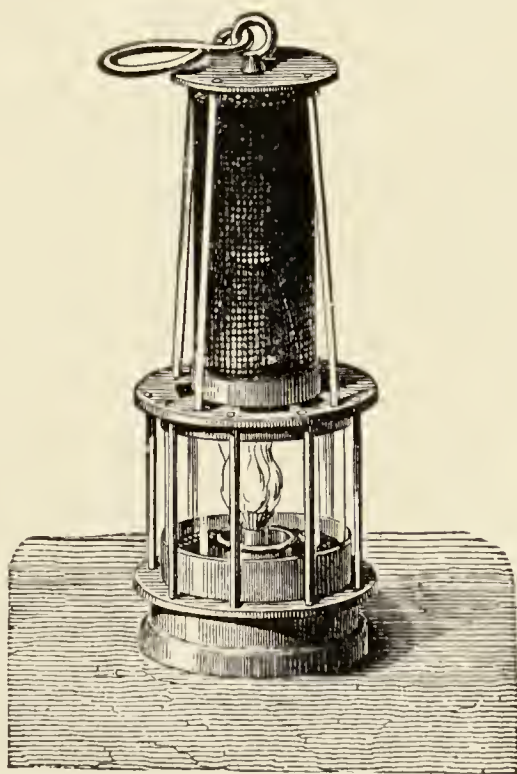


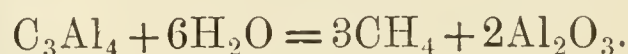
FIG. 69.—Davy safety-lamp.
[Modern form.]

Sir Humphry Davy observed that on introducing a piece of wire gauze into a flame, it absorbs so much heat that combustion does not proceed beyond it (the unburnt gases which pass through it may be ignited on the other side). In accordance with this, the flame of the Davy lamp is surrounded with a thick glass (as shown in the drawing), and has no communication whatever with the explosive mixture except through a wire gauze which prevents it igniting the mixture of the marsh gas, issuing from the coal, with air. In some districts, particularly in those where petroleum is found—as, for instance, near Baku, where a temple of the Indian fire-worshippers was built, and in Pennsylvania, and other places—marsh gas in abundance issues from the earth, and is used, like coal gas, for the purposes of lighting and warming.³⁴ Tolerably pure marsh gas may be obtained by heating a mixture of an acetate with an alkali. Acetic acid, $C_2H_4O_2$, on being heated is decomposed into marsh gas and carbonic anhydride, $C_2H_4O_2 = CH_4 + CO_2$.

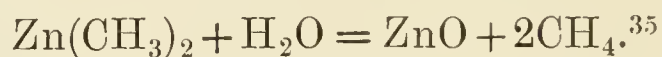
An alkali—for instance, $NaHO$ —gives with acetic acid a salt, $C_2H_3NaO_2$, which on decomposition retains carbonic anhydride, forming sodium carbonate, Na_2CO_3 , and marsh gas is given off :



Carbide of aluminium, Al_4C_3 , prepared by the direct action of charcoal on aluminium in the heat of the voltaic arc (in the electric furnace), gives methane and alumina in the form of hydrate when acted upon by water :



The purest gas is obtained from methyl iodide, CH_3I (prepared by the action of HI on methyl, or wood, alcohol), by the substitution of the iodine by hydrogen, which is done, for instance, by taking zinc dust and alcohol or ready-made zinc methyl and water :



Marsh gas is difficult to liquefy ; it is almost insoluble in water, and is without taste or smell. The most important point in connection

cylinder which is firmly held in a metallic holder. Over this a metallic cylinder and the wire gauze are placed. The products of combustion pass through the gauze, and the air enters through the space between the cylinder and the wire gauze. To ensure greater safety the lamp cannot be opened without extinguishing the flame.

³⁴ In Pennsylvania (beyond the Alleghany Mountains) many of the shafts sunk for petroleum only emitted gas, but many useful applications for it were found and it was conducted in metallic pipes to works hundreds of miles distant, principally for metallurgical purposes. Natural gas is also beginning to be used at Baku.

³⁵ Details of the methods of preparation and reactions of CH_4 , $Zn(CH_3)_2$, CH_3I , and other carbon compounds must be sought in text-books of organic chemistry.

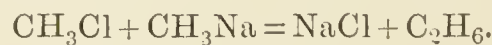
with its chemical reactions is that it does not combine directly with anything, whilst the other hydrocarbons which contain less hydrogen than is expressed by the formula C_nH_{2n+2} are capable of combining with hydrogen, chlorine, certain acids, &c.

While the law of substitution gives a very simple explanation of the formation of hydrogen peroxide as a compound containing two aqueous residues (OH)(OH), and while the same conceptions explain all the transitions from ammonia to nitric acid with great simplicity, it is possible also, on the basis of this law, to derive all hydrocarbons from methane, CH_4 , as being the simplest hydrocarbon.³⁶ The increase in complexity of a molecule of methane is brought about by the faculty of mutual combination possessed by the atoms of carbon, and, as a consequence of the most detailed study of the subject, much that might have been foreseen and conjectured from the law of substitution has been actually brought about; and although this subject on account of its magnitude really belongs, as has been already stated, to the sphere of organic chemistry, it has been alluded to here in order to show, although only in part, the best investigated example of the application of the law of substitution. According to the law of substitution, a molecule of methane, CH_4 , is capable of undergoing substitution in the four following ways:—(1) *Methyl substitution*, when the radicle, equivalent to hydrogen, called **methyl**, CH_3 , replaces hydrogen. In CH_4 this radicle is combined with H, and therefore can replace it, as (OH) replaces H, because it gives with it water; (2) *methylene substitution*, or the exchange between H_2 and CH_2 (this radicle is called methylene), is founded on a similar division of the molecule CH_4 into two equivalent parts, H_2 and CH_2 ; (3) *acetylene substitution*, or the exchange between CH on the one hand and H_3 on the other; and (4) *carbon substitution*—that is, the substitution of H_4 by an atom of carbon C, which is founded on the law of substitution, just as is the methyl substitution. These four cases of substitution render it possible to understand the principal relations of the hydrocarbons and of their products (derivatives). For instance, the *law of even numbers* is seen from the fact that in all the cases of substitution mentioned the hydrogen atoms increase or decrease by an even number; but as in CH_4 they are likewise even, it follows that no matter how many substitutions are effected there will always be obtained an even number of hydrogen atoms. When H is replaced by CH_3 there is an increase of CH_2 ; when H_2 is replaced by CH_2 there is no increase of hydrogen; in the acetylene

³⁶ Methylene, CH_2 , does not exist. When attempts are made to obtain it (for example, by removing X_2 from CH_2X_2), C_2H_4 or C_3H_6 are produced—that is to say, it undergoes polymerisation.

substitution CH replaces H_3 , so that there is an increase of C and a decrease of H_2 ; in the carbon substitution there is a decrease of H_4 . In a similar way the *law of limits* may be deduced as a corollary of the law of substitution. For the largest possible quantity of hydrogen is introduced by the methyl substitution, since it leads to the addition of CH_2 ; starting from CH_4 we obtain C_2H_6 , C_3H_8 , and in general, C_nH_{2n+2} , and these contain the greatest possible amounts of hydrogen. *Unsaturated hydrocarbons*, containing less hydrogen, are evidently only formed when the increase of the new molecule derived from methane proceeds from one of the other forms of substitution. When the methyl substitution alone takes place in methane, CH_4 , it is evident that the saturated hydrocarbon formed is C_2H_6 or $(CH_3)(CH_3)$.³⁷ This is called **ethane**. By means of the methylene substitution alone, **ethylene**, C_2H_4 , or $(CH_2)(CH_2)$, may be directly obtained from CH_4 , and by the acetylene substitution C_2H_2 or $(CH)(CH)$, or **acetylene**, both the latter being unsaturated hydrocarbons. Thus we have *all the possible* hydrocarbons with two atoms of carbon in the molecule, C_2H_6 , ethane, C_2H_4 , ethylene, and C_2H_2 , acetylene. But in them, according to the law of substitution, the same forms of substitution may be repeated, and further substitutions will hence serve as a source for the production of a fresh series of saturated and unsaturated hydrocarbons, containing more and more carbon in the molecule and, in the case of the acetylene substitution and carbon substitution, containing less and less hydrogen. Thus *by means of the law of substitution we can foresee* not only the limit C_nH_{2n+2} , but an *unlimited number of unsaturated hydrocarbons*, C_nH_{2n} , C_nH_{2n-2} . . . $C_nH_{2(n-m)}$, where m varies from 0 to $n-1$,³⁸ and where n increases indefinitely. From these facts not only does the

³⁷ Although the methods of formation and the reactions connected with hydrocarbons are not described in this work, because they are dealt with in organic chemistry, yet in order to clearly show the mechanism of those transformations by which the carbon atoms are built up into the molecules of the carbon compounds, we here give a general example of reactions of this kind. From marsh gas, CH_4 , on the one hand the substitution of chlorine or iodine, CH_3Cl , CH_3I , for the hydrogen may be effected; and on the other hand such metals as sodium and zinc may be substituted for the hydrogen, giving, e.g., CH_3Na , $Zn(CH_3)_2$. These and similar products of substitution serve as a means of obtaining other more complex substances from given carbon compounds. If we place the two above-named products of substitution of marsh gas (metallic and haloid) in mutual contact, the metal combines with the halogen, forming a very stable compound—namely, common salt, $NaCl$, and the carbon groups which were in combination with them separate in mutual combination, as shown by the equation:



This is the most simple example of the formation of a complex hydrocarbon from these radicles.

³⁸ When $m = n - 1$, we have the series C_nH_{2n-2} . The lowest member is acetylene, C_2H_2 . These are hydrocarbons containing a minimum amount of hydrogen.

existence of a multitude of polymeric hydrocarbons, differing in molecular weight, become intelligible, but it is also seen that there is a possibility of cases of isomerism with the same molecular weight. This **polymerism** so common to hydrocarbon compounds is already apparent in the first unsaturated series C_nH_{2n} , because all the terms of this series C_2H_4 , C_3H_6 , C_4H_8 . . . $C_{30}H_{60}$. . . have one and the same composition, CH_2 , but different molecular weights, as has been already explained in Chapter VII. The differences in the vapour densities, boiling-points, melting-points, the quantities entering into reactions,³⁹ and the methods of preparation⁴⁰ also so clearly tally with the conception of polymerism, that this example will always be the clearest and most conclusive for the illustration of polymerism and molecular weight. Such a case is also met with among other hydrocarbons. Thus benzene, C_6H_6 , and cinnamene, C_8H_8 , correspond with the composition of acetylene or with a compound of the composition, CH .⁴¹ The first boils at 81° , the second at 144° ; the specific gravity of the first at 0° is 0.899, that of the second, 0.925—that is, here also the boiling-point rises with the increase of molecular weight, and so also, as might be expected, does the density.

Cases of **isomerism** in the restricted sense of the word—that is, when, with an identity of composition and molecular weight, the properties of the substances are different—are very numerous among the hydrocarbons and their derivatives. Such cases are particularly important for the comprehension of molecular structure, and they also, like the polymerides, may be predicted from the above-mentioned conceptions, expressing the principles of the structure of the carbon compounds⁴² based on the law of substitution. According to it, for

³⁹ For instance, ethylene, C_2H_4 , combines with Br_2 , HI , H_2SO_4 , as a whole molecule, as also does amylene, C_5H_{10} , and, in general, C_nH_{2n} .

⁴⁰ For instance, ethylene is obtained by removing the water from ethyl alcohol, $C_2H_5(OH)$, and amylene, C_5H_{10} , from amyl alcohol, $C_5H_{11}(OH)$, or in general C_nH_{2n} from $C_nH_{2n+1}(OH)$.

⁴¹ Acetylene and its polymerides have an empirical composition CH , ethylene and its homologues (and polymerides) CH_2 , ethane CH_3 , methane CH_4 . This series presents a good example of the law of multiple proportions, but such diverse proportions are met with between the number of atoms of the carbon and hydrogen in the hydrocarbons already known that the accuracy of Dalton's law might be doubted. Thus the substances $C_{30}H_{62}$ and $C_{30}H_{60}$ have such slight differences in their composition by weight as to be within the limits of experimental error, but their reactions and properties are so distinct that they can, however, be distinguished beyond doubt. Without Dalton's law chemistry could not have been brought to its present condition, but it cannot alone express all those gradations which are quite clearly understood and predicted by the law of Avogadro-Gerhardt.

⁴² The conception of the structure of carbon compounds—that is, the expression of those unions and correlations which their atoms have in the molecules—was for a long time limited to the representation that organic substances contained complex radicles

example, it is evident that there can be no isomerism in the cases of the saturated hydrocarbons C_2H_6 and C_3H_8 , because the former is CH_4 , in which methyl has taken the place of H, and as all the hydrogen atoms of methane must be supposed to have the same relation to the carbon, it is all the same which of them be subjected to the methyl substitution—the resulting product can only be ethane, CH_3CH_3 ; ⁴³ the same argument also applies in the case of propane, $CH_3CH_2CH_3$, where one compound only can be imagined. It is to be expected, however, that there should be two butanes, C_4H_{10} , and this is actually the case. In one, methyl may be considered as replacing the hydrogen of one of the methyls, $CH_3CH_2CH_2CH_3$; and in the other CH_3 may be considered as substituted for H in CH_2 , and there it will consist of $CH_3CH \begin{smallmatrix} CH_3 \\ CH_3 \end{smallmatrix}$. The latter may also be regarded as methane in which three of hydrogen are exchanged for three of methyl. On going further in the series it is evident that the number of possible isomerides will be still greater, but we have limited ourselves to the simplest examples, showing the possibility and actual existence of isomerides. C_2H_4 and CH_2CH_2 are, it is evident, identical; but there ought to be, and are, two hydrocarbons of the composition C_3H_6 , propylene and trimethylene; the first is ethylene,

(for instance, ethyl C_2H_5 , methyl CH_3 , phenyl C_6H_5 , &c.); then about the year 1840 the phenomena of substitution and the correspondence of the products of substitution with the primary bodies (nuclei and types) were observed, but it was not until about the year 1860 and later when, on the one hand, the teaching of Gerhardt about molecules was spreading, and, on the other, the materials had accumulated for discussing the transformations of the simplest hydrocarbon compounds, that conjectures began to appear as to the mutual connection of the atoms of carbon in the molecules of the complex hydrocarbon compounds. Then Kekulé and A. M. Butleroff began to formulate the connection between the separate atoms of carbon, regarding it as a quadrivalent element. Although in their methods of expression and in some of their views they differ from each other and also from the way in which the subject is treated in this work, yet the essence of the matter—namely, the comprehension of the causes of isomerism and of the union between the separate atoms of carbon—remains the same. In addition to this, starting from the year 1870, there appears a tendency, which from year to year increases, to discover the actual spacial distribution of the atoms in the molecules. Thanks to the endeavours of Le-Bel (1874), van't Hoff (1874), and Wislicenus (1887) in observing cases of isomerism—such as the effect of different isomerides on the direction of the rotation of the plane of polarisation of light—this tendency promises much for chemical mechanics, but the details of the still imperfect knowledge in relation to this matter must be sought for in special works devoted to organic chemistry.

⁴³ Direct experiment shows that however CH_3X is prepared (where X=for instance Cl, &c.) it is always one and the same substance.

This was shown in the year 1860, or thereabout, by many methods, and is the fundamental conception of the structure of hydrocarbon compounds. If the atoms of hydrogen in methane were not absolutely identical in value and position (as they are not, for instance, in $CH_3CH_2CH_3$ or CH_3CH_2X), then there would be as many different forms of CH_3X as there were diversities in the atoms of hydrogen in CH_4 .

CH_2CH_2 , in which one atom of hydrogen is exchanged for methyl, CH_2CHCH_3 , and trimethylene is ethane, CH_3CH_3 , with the substitution of methylene for two hydrogen atoms from two methyl groups—that is, $\begin{smallmatrix} \text{CH}_2 \\ \text{CH}_2 \end{smallmatrix} \text{CH}_2$,⁴⁴ where the methylene introduced is united to both the atoms of carbon in CH_3CH_3 . It is evident that the cause of isomerism here is, on the one hand, the difference of the amount of hydrogen in union with the particular atoms of carbon, and, on the other, the different connection between the several atoms of carbon. In the first case they may be said to be chained together (more usually to form an ‘open chain’), and in the second case to be locked together (to form a ‘closed chain’ or ‘ring’). Here also it is easily understood that on increasing the number of carbon atoms the number of possible and existing isomerides will greatly increase. If, at the same time, in addition to the substitution of one of the radicles of methane for hydrogen a further exchange of part of the hydrogen for some of the other groups of elements X, Y . . . occurs, the number of possible isomerides still further increases in a considerable degree. For instance, there are even two possible isomerides for the derivatives of ethane, C_2H_6 : if two atoms of the hydrogen be exchanged for X_2 , one will have the ethylene structure, $\text{CH}_2\text{XCH}_2\text{X}$, and the other an ethylidene structure, CH_3CHX_2 ; such are, for instance, ethylene chloride, $\text{CH}_2\text{ClCH}_2\text{Cl}$, and ethylidene chloride, CH_3CHCl_2 . And as in the place of the hydrogen not only metals may be substituted, but Cl, Br, I, OH (the water radicle), NH_2 (the ammonia radicle), NO_2 (the radicle of nitric acid), &c., so also in exchange for two atoms of hydrogen, O, NH, S, &c., may be substituted; hence it will be understood that the number of isomerides is sometimes very great. It is impossible here to describe how the isomerides are distinguished from each other, in what reactions they occur, how and when one changes into another, &c.; for this, taken together with the description of the hydrocarbons already known, and their derivatives, forms a very extensive and very thoroughly investigated branch of chemistry, called **organic chemistry**. Enriched with a mass of closely observed phenomena and strictly deduced generalisations, this branch of chemistry has been treated separately for the reason that in it the hydrocarbon groups are subjected to transformations which are not met with in such number in dealing with any of the other elements or their hydrogen compounds. It was important for us to show that,

⁴⁴ The union of carbon atoms in closed chains or rings was first suggested by Kekulé as an explanation of the structure and isomerism of the derivatives of benzene, C_6H_6 , forming aromatic compounds (note 26).

notwithstanding the great variety of the hydrocarbons and their products,⁴⁵ they are all of them governed by the law of substitution,^{45a} and, referring our readers for detailed information to works on organic chemistry, we will limit ourselves to a short exposition of the properties of the two simplest unsaturated hydrocarbons: ethylene, CH_2CH_2 , and acetylene, CHCH , and a short acquaintance with petroleum as the natural source of a mass of hydrocarbons.

Ethylene, or olefiant gas, C_2H_4 , is the lowest known member of the unsaturated hydrocarbon series of the composition C_nH_{2n} . As in composition it is equal to two molecules of marsh gas deprived of two molecules of hydrogen, it is evident that it might be, and it actually can be, produced, although but in small quantities, together with hydrogen, by heating marsh gas. On being heated, however, olefiant gas splits up, first into acetylene and methane ($3\text{C}_2\text{H}_4 = 2\text{C}_2\text{H}_2 + 2\text{CH}_4$,

⁴⁵ The following are the most generally known of the oxygenised but non-nitrogenous hydrocarbon derivatives. (1) The *alcohols*. These are hydrocarbons in which hydrogen is exchanged for hydroxyl (OH). The simplest of them is methyl alcohol, $\text{CH}_3(\text{OH})$, or wood spirit, obtained by the dry distillation of wood. The common spirits of wine or ethyl alcohol $\text{C}_2\text{H}_5(\text{OH})$, and glycol, $\text{C}_2\text{H}_4(\text{OH})_2$, correspond with ethane. Normal propyl alcohol $\text{CH}_3\text{CH}_2\text{CH}_2(\text{OH})$, and isopropyl alcohol, $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$, *propylene-glycol*, $\text{C}_3\text{H}_6(\text{OH})_2$, and glycerol, $\text{C}_3\text{H}_5(\text{OH})_3$ (which, with stearic and other acids, forms fatty substances), correspond with propane, C_3H_8 . All alcohols are capable of forming water and *ethereal salts* with acids, just as alkalies form ordinary salts. (2) *Aldehydes* are alcohols minus hydrogen; for instance, acetaldehyde, $\text{C}_2\text{H}_4\text{O}$, corresponds with ethyl alcohol. (3) It is simplest to regard *organic acids* as hydrocarbons in which hydrogen has been exchanged for carboxyl (CO_2H), as will be explained in the following chapter. There are a number of intermediate compounds; for example, the aldehyde-alcohols, alcohol-acids (or hydroxy-acids), &c. Thus the hydroxy-acids are hydrocarbons in which some of the hydrogen has been replaced by hydroxyl, and some by carboxyl; for instance, lactic acid corresponds with C_2H_6 , and has the constitution $\text{C}_2\text{H}_4(\text{OH})(\text{O}_2\text{H})$. If to these products we add the haloid salts (where H is replaced by Cl, Br, I), the nitro-compounds containing NO_2 in place of H, the amides, cyanides, ketones, and other compounds, it will be readily seen what an immense number of organic compounds there are and what a variety of properties these substances have; this we see also from the composition of plants and animals.

^{45a} In this and other portions of my work I refrain from introducing the usual and, to many chemists, customary notion of the atomicity or equivalency of the elements, and give the law of substitution and its consequences instead. This is done chiefly for two reasons: (1) the equivalency of the elements (for instance, 4 for C, 2 for O, &c.) cannot be regarded as one of their radical, unchangeable properties (see Chapter X., note 1), and the principal object of this work is to embrace the unchanging fundamental properties of the chemical elements; (2) the law of substitution, being a direct application of one of the Newtonian principles of all natural philosophy (action and reaction are equal and opposite), gives the possibility of understanding sufficiently, and without any supplementary hypothesis, all that the conception of equivalency gives, even in such an instance as the carbon (organic) compounds in which it first took rise and was most frequently and successfully applied. Moreover, I think that the student who has grasped the law of substitutions will encounter no difficulty in grasping the conception of atomicity (for instance, of carbon), but will rather regard the matter from a wider and freer point of view by the light cast upon it by the law of substitution.

Lewes, 1894), and at a higher temperature into carbon and hydrogen ; and therefore in those cases where marsh gas is produced by heating, olefiant gas, hydrogen, and charcoal will also be formed, although only in small quantities. The lower the temperature at which complex organic substances are heated, the greater the quantity of olefiant gas found in the gases given off ; at a white heat it is entirely decomposed into charcoal and marsh gas. If coal, wood, and more particularly petroleum, tars, and fatty substances are subjected to dry distillation, they give off illuminating gas, which contains more or less olefiant gas.

Olefiant gas, almost free from other gases,⁴⁶ may be obtained from ordinary alcohol (if possible, free from water) if the latter be mixed with five parts of strong sulphuric acid and the mixture heated to slightly above 100°. Under these conditions, the sulphuric acid removes the elements of water from the alcohol, $C_2H_5(OH)$, and gives olefiant gas : $C_2H_6O = H_2O + C_2H_4$. The greater molecular weight of olefiant gas compared with that of marsh gas indicates that it may be comparatively easily converted into a liquid by means of pressure of great cold ; this may be effected, for example, by the evaporation of liquid nitrous oxide. Its absolute boiling-point is + 10°, it boils at - 103° (1 atmosphere), liquefies at 0°, at a pressure of 43 atmospheres, and solidifies at - 163°. Ethylene is colourless, has a slight ethereal smell, is slightly soluble in water, and somewhat more soluble in alcohol and in ether (in five volumes of spirit or six volumes of ether).⁴⁷

Like other unsaturated hydrocarbons, olefiant gas readily enters into combination with certain substances, such as chlorine, bromine, iodine, fuming sulphuric acid, or sulphuric anhydride, &c. If olefiant gas be sealed up with a small quantity of sulphuric acid in a glass vessel, and constantly agitated (as, for instance, by attaching it to the

⁴⁶ Ethylene bromide, $C_2H_4Br_2$, when gently heated in alcoholic solution with finely divided zinc, yields pure ethylene, the zinc merely taking up the bromine (Sabaneyeff).

⁴⁷ Ethylene decomposes somewhat easily under the influence either of the electric spark or of a high temperature. In this case the volume of the gas formed may remain the same when olefiant gas is decomposed into carbon and marsh gas, or may increase to double its volume when hydrogen and carbon are formed, $C_2H_4 = CH_4 + C = 2C + 2H_2$. A mixture of olefiant gas and oxygen is highly explosive; two volumes of this gas require six volumes of oxygen for their perfect combustion. The eight volumes thus taken then resolve themselves into eight volumes of the products of combustion, a mixture of water and carbonic anhydride, $C_2H_4 + 3O_2 = 2CO_2 + 2H_2O$. On cooling after the explosion diminution of volume occurs because the water becomes liquid. For two volumes of the olefiant gas taken, the diminution will be equal to four volumes, and the same is the case for marsh gas. The quantities of carbonic anhydride formed by the two gases are not the same. Two volumes of marsh gas give only two volumes of carbonic anhydride, whilst two volumes of ethylene give four volumes of carbonic anhydride. In the presence of platinum black, a mixture of C_2H_4 and H_2 contracts owing to the formation of ethane, C_2H_6 (Lunge, 1897).

moving part of a machine), the prolonged contact and repeated mixing causes the olefiant gas, little by little, to combine with the sulphuric acid, forming $C_2H_4H_2SO_4$. If, after this absorption, the sulphuric acid be diluted with water and distilled, alcohol will be produced by the olefiant gas combining with the elements of water, $C_2H_4 + H_2O = C_2H_6O$. In this reaction (Berthelot) we see an excellent example of the fact that if a given substance, like olefiant gas, is produced by the decomposition of another, then in the reverse way this substance, entering into combination, is capable of forming the original substance—in our example, alcohol. In combination with various molecules, X_2 , ethylene gives saturated compounds, $C_2H_4X_2$ or CH_2XCH_2X (for example, $C_2H_4Cl_2$), which correspond with ethane, CH_3CH_3 or C_2H_6 .⁴⁸

Acetylene, $C_2H_2 = CHCH$, is a gas; it was first prepared by Berthelot (1857). It has a very pungent smell, is characterised by its great stability under the action of heat, and is obtained as the only product of the direct combination of carbon with hydrogen when a luminous arc (voltaic) is formed between carbon electrodes in an atmosphere of hydrogen. This arc contains particles of carbon passing from one pole to the other. Acetylene may be formed from olefiant gas if two atoms of hydrogen be taken from it. This may be effected in the following way: the olefiant gas is first made to combine with bromine, giving $C_2H_4Br_2$; from this hydrobromic acid is removed by means of an alcoholic solution of caustic potash, leaving the volatile product C_2H_3Br ; and from this yet another molecule of hydrobromic acid is withdrawn by passing it through anhydrous alcohol in which metallic sodium has been dissolved, or by heating it with a strong alcoholic solution of caustic potash. Under these circumstances (Berthelot, Sawitsch, Miasnikoff) the alkali takes up the hydrobromic acid from $C_nH_{2n-1}Br$, forming C_nH_{2n-2} .

Acetylene is obtained for lighting purposes (for bicycles and carriages) by the action of water on the carbide (carbon compound) of calcium, CaC_2 (Chapter XIV.), formed by the action of charcoal on lime in the electric furnace.^{48a} It is also produced by the imperfect

⁴⁸ The homologues of ethylene, C_nH_{2n} , are also capable of direct combination with halogens, &c., but with various degrees of facility. The composition of these homologues can be expressed thus: $(CH_3)_x(CH_2)_y(CH)_zC_r$, where the sum of x and z is always an even number, and $x + z + r$ is equal to half of $3x + z$, whence $z + 2r = x$; by this means the possible isomerides are determined. For example, for butylenes, C_4H_8 , $(CH_3)_2(CH)_2$, $(CH_3)_2(CH_2)C$, $(CH_3)(CH_2)_2CH$, and $(CH_2)_4$ are possible.

^{48a} It must be remembered in using acetylene that it is poisonous and explosive, not only in admixture with air, but spontaneously ($C_2H_2 = C_2 + H_2$) under the action of electric sparks, a blow, or concussion. The explosion of liquid (absolute boiling-point $+37^\circ$) and compressed acetylene is especially dangerous. It is very soluble in acetone (25 vols.

combustion of olefiant and marsh gases—for example, if the flame of coal gas has not free access to air.⁴⁹

Acetylene, being further removed than ethylene from the limit C_nH_{2n+2} of hydrocarbon compounds, has a still greater faculty of combination than is shown by olefiant gas, and therefore can be more readily separated from any mixture containing it. Actually, acetylene not only combines with one and two molecules of I_2 , HI , H_2SO_4 , Cl_2 , Br_2 , &c. (many other unsaturated hydrocarbons also combine with them), but also with cuprous chloride, $CuCl$, forming a red precipitate. If a gaseous mixture containing acetylene be passed through an ammoniacal solution of cuprous chloride (or silver nitrate), the other gases do not combine, but the acetylene gives a red precipitate (or grey with silver), which detonates when struck with a hammer. This red precipitate gives off acetylene under the action of acids. In this manner pure acetylene may be obtained. Acetylene and its homologues also readily react with corrosive sublimate, $HgCl_2$ (Koucheroff, Favorsky). Acetylene burns with a very brilliant flame, which is accounted for by the comparatively large amount of carbon it contains, and which is taken advantage of in its employment for lighting purposes. For this purpose the acetylene is prepared in a closed vessel by the action of water on C_2Ca , and escapes under pressure through a fine orifice, where it is lighted.⁵⁰

The formation and existence in nature of large masses of **petroleum**, which is a mixture of liquid hydrocarbons, principally of the series C_nH_{2n} , C_nH_{2n+2} is in many respects remarkable.⁵¹ In some mountainous

under the ordinary pressure), and even water dissolves it (up to 50 per cent.) in greater quantity than any other hydrocarbon gas, probably owing to its presenting the germs of an acid character (see Chap. XIV., note 62: C_2H_2 , C_2HNa , C_2Na_2 , C_2Ca).

⁴⁹ This is easily accomplished with those gas burners which are used in laboratories and mentioned in the Introduction. In these burners the gas is first mixed with air in a long tube, above which it is kindled. But if it be lighted inside the pipe, it does not burn completely, but forms acetylene on account of the cooling effect of the walls of the metallic tube; this is detected by the smell, and may be shown by passing the issuing gas (by aid of an aspirator) into an ammoniacal solution of cuprous chloride.

⁵⁰ The area of the orifice for the escape of the gas is 15–25 times smaller than in the ordinary gas burner. Amongst the homologues of acetylene C_nH_{2n-2} , the lowest is C_3H_4 ; the isomerides allylene, CH_3CCH , and allene, CH_2CCH_2 , are known, as well as $CH_2(CH)_2$, having a closed structure.

⁵¹ The saturated hydrocarbons predominate in American petroleum, especially in the more volatile portions; in Baku naphtha, hydrocarbons of the composition C_nH_{2n} form the main part (Lisenko, Markovnikoff, Beilstein), but doubtless (Mendeléeff) it also contains saturated ones, C_nH_{2n+2} . The structure of the naphtha hydrocarbons is only known for the lower homologues, but doubtless the distinction between the hydrocarbons of the Pennsylvania and Baku naphthas, boiling at the same temperature (after the requisite refining by repeated fractional distillation, which can be very conveniently done by means of steam rectification—that is, by passing steam through the dense mass), depends not only on the predominance of saturated hydrocarbons in the former,

districts—as, for instance, by the slopes of the Caucasian chain, on inclines lying in a direction parallel to the range—an oily combustible liquid issues from the earth together with salt water and hot gases (methane and others); it has a tarry smell and dark brown colour, and is lighter than water. This liquid is called naphtha or rock oil (petroleum) and is obtained in large quantities by sinking wells and deep bore-holes in those places where traces of naphtha^{51a} are observed, the naphtha being sometimes thrown up from the wells in fountains of considerable height.⁵² The evolution of naphtha is always accompanied by salt water and marsh gas. Naphtha has from ancient times been worked in Russia in the Apsheron peninsula near Baku, and is also now worked in Burmah (India), in Galicia near the Carpathians, and in America, especially in Pennsylvania and Canada, &c. Naphtha does not consist of one definite hydrocarbon, but of a mixture of several, and its density, external appearance, and other properties vary with the amounts of the different hydrocarbons of which it is composed. The light kinds of naphtha have a specific gravity about 0·8 and the heavy kinds up to 0·98. The former are very mobile liquids, and more volatile; the latter contain less of the volatile hydrocarbons and are less mobile. When the light kinds of naphtha are distilled, the boiling-point taken in the vapours constantly changes, beginning at 0° and going up to above 350°. That which passes over first is a very mobile, colourless ethereal liquid (forming gasolene, ligroin, benzoline, &c.), from which the hydrocarbons whose boiling-points start from 0° may be extracted—namely, the hydrocarbons C_4H_{10} , C_5H_{12} (which boils at 30°), C_6H_{14} (boiling at about 62°), C_7H_{16} (boiling about 90°), &c. Those fractions of the naphtha distillate which boil above 130°, and

and naphthenes, C_nH_{2n} , in the latter, but also on the diversity of composition and structure of the corresponding portions of the distillation. The products of the Baku naphtha are richer in carbon (therefore in a suitably constructed lamp they ought to give a brighter light) and of greater specific gravity, and have greater internal friction (and are therefore more suitable for lubricating machinery) than the American products collected at the same temperature.

^{51a} In all probability deep bore-holes would prove the presence of naphtha where no signs of it are to be seen on the surface, because some mountain chains have been levelled in the course of time, and the naphtha may remain unchanged for any period surrounded by clay strata in the depths of the earth.

⁵² The formation of naphtha fountains (which sometimes burst forth after the higher clay strata covering the layers of sands impregnated with naphtha have been bored through) is without doubt caused by the pressure or tension of the combustible hydrocarbon gases which accompany the naphtha, and are soluble in it under pressure. Sometimes these naphtha fountains reach a height of 100 metres—for instance, the fountain of 1887 near Baku. Naphtha fountains generally act periodically, and their force diminishes with the lapse of time, as might be expected, because the gases which cause the fountains find an outlet, the naphtha issuing from the bore-hole carrying away the sand which was partially choking it up.

contain hydrocarbons with C_9 , C_{10} , C_{11} , &c., enter into the composition of the oily substance, universally used for lighting, called *kerosene*, *photogen*, *photonaphthalene*, and other names. The specific gravity of kerosene is from 0.77 to 0.84, and it smells like naphtha. Those products of the distillation of naphtha which pass off below 130° and have a specific gravity below 0.75, enter into the composition of light petroleum (benzoline, ligroin, petroleum spirit, &c.), which is used as a solvent for india-rubber, for removing grease-spots, and as a fuel for motors (bicycles, &c.) and other purposes. Those portions of naphtha (which can only be distilled without change by means of superheated steam, otherwise they are largely decomposed) which boil above 275° and up to 300° , and have a specific gravity higher than 0.84, form an excellent oil,⁵³ safe as regards inflammability (which is very important, as it diminishes the risks of fire), and may be used in lamps as an effective substitute for kerosene.⁵⁴ Those portions of naphtha which pass over at a still higher temperature and have a higher specific gravity than 0.9, which are found in abundance (about 30 per cent.) in the

⁵³ This is a so-called intermediate oil (between kerosene and lubricating oils), solar oil, or *pyronaphtha*. Lamps are already being manufactured for burning it, but they still require improvement. Above all, however, it requires a more extended market, and this at present is wanting, owing to the two following reasons: (1) Those products of the American petroleum which are the most widely spread and almost universally consumed contain but little of this intermediate oil, and what there is is divided between the kerosene and the lubricating oils; (2) the Baku naphtha, which is capable of yielding a great deal (up to 30 per cent.) of intermediate oil, is produced in enormous quantities, about 500 million poods, but has no regular markets abroad, and for the consumption in Russia (about 35 million poods of kerosene per annum) and for the limited export (80 million poods per annum) into Western Europe (by the Trans-Caucasian Railway) those volatile and more dangerous parts of the naphtha which enter into the composition of the American petroleum are sufficient, although Baku naphtha yields about 25 per cent. of such kerosene. For this reason pyronaphtha is not manufactured in sufficient quantities, and the whole world is consuming the unsafe kerosene. When a pipe line has been laid from Baku to the Black Sea (in America there are many which carry the raw naphtha to the sea-shore, where it is made into kerosene and other products) then the whole mass of the Baku naphtha will furnish safe illuminating oils, which without doubt will find an immense application. A mixture of the intermediate oil with kerosene or Baku oil (specific gravity 0.84 to 0.85) may be considered (on removing the benzoline) to be the best illuminating oil, because it is safe (flashing point from 40° to 60°), cheaper (Baku naphtha gives as much as 60 per cent. of Baku oil), and burns perfectly well in lamps differing but little from those everywhere made for burning American kerosene (unsafe, flashing-point 20° to 30°).

⁵⁴ The substitution of Baku pyronaphtha, or intermediate oil, or Baku oil (see note 53), would not only be a great advantage as regards safety from fire, but would also be highly economical. A ton (61 poods) of American crude petroleum costs at the coast considerably more than 24s. (12 roubles), and yields two-thirds of a ton of kerosene suitable for ordinary lamps. A ton of raw naphtha in Baku costs from 6s. to 12s. (3 to 6 roubles), and with a pipe line to the shore of the Black Sea would not cost more than 8 roubles, or 16s. Moreover, a ton of Baku naphtha will yield as much as two-thirds of a ton of kerosene, Baku oil, and pyronaphtha suitable for illuminating purposes.

Baku naphtha, make excellent lubricating or machine oils. The remaining tar, on distillation with superheated steam (at about 410°), decomposes, giving vaseline (used in pomades, plasters, &c., and forming a kind of cerate). Naphtha has thus many important applications, and the naphtha industry is now of great commercial importance, especially as naphtha and its refuse may be used as fuel.⁵⁵ Whether naphtha was formed from organic matter is very doubtful, as it is found in the most ancient Silurian strata which correspond with epochs of the earth's existence when but little organic matter existed; it could not penetrate from the higher to the lower (more ancient) strata, as it floats on water (and water penetrates through all strata). It therefore tends to rise to the surface of the earth, and it is found in highlands parallel to the direction of the mountains.⁵⁶ Much

⁵⁵ Naphtha has been applied for heating purposes on a large scale in Russia, not only on account of the low cost of naphtha itself and of the *residue* from the preparation of kerosene, but also because the products of all the Baku naphtha do not find an outlet for general consumption, and the only railway across the Caucasus is unable to carry 300–400 million poods a year. Naphtha itself and its various residues form excellent fuel, burning without smoke and giving a high temperature (steel and iron may be easily melted in the flame). A hundred poods of good coal (for instance, Don coal) used as fuel for heating boilers are equivalent to 36 cubic feet (about 250 poods) of dry wood, while only 70 poods of naphtha would be required to give the same effect; and moreover there is no need for stoking, as the liquid can be readily and evenly supplied in the required quantity. The economic and other questions relating to American and Baku petroleum have been discussed more in detail in some separate works of mine (D. Mendeléeff): (1) *The Naphtha Industry of Pennsylvania and the Caucasus*, 1870; (2) *Where to build Naphtha Works*, 1880; (3) *On the Naphtha Question*, 1883; (4) *The Baku Naphtha Question*, 1886; (5) the article on the naphtha industry in the account of the Russian industries printed for the Chicago Exhibition.

⁵⁶ As during the process of the dry distillation of wood, seaweed, and similar vegetable *débris*, and also when fats are decomposed by the action of heat (in closed vessels), hydrocarbons similar to those of naphtha are formed, it was natural that this fact should have been turned to account to explain the formation of the latter. But the hypothesis of the formation of naphtha from vegetable *débris* inevitably assumes coal to be the chief element of decomposition, and naphtha is met with in Pennsylvania and Canada, in the Silurian and Devonian strata, which do not contain coal, and correspond to an epoch not abounding in organic matter. Coal was formed from the vegetable *débris* of the Carboniferous, Jurassic, and other recent strata, but judging more from its composition and structure, it has been subjected to the same kind of decomposition as peat; nor could liquid hydrocarbons have been thus formed to such an extent as we see in naphtha. If we ascribe the derivation of naphtha to the decomposition of fat (adipose, animal fat) we encounter three almost insuperable difficulties: (1) Animal remains would furnish a great deal of nitrogenous matter, whilst there is but very little in naphtha; (2) the enormous quantity of naphtha already discovered as compared with the insignificant amount of fat in the animal carcase; (3) the sources of naphtha always running parallel to mountain chains is completely inexplicable. Being struck with this last-mentioned circumstance in Pennsylvania, and finding that the sources in the Caucasus surround the whole Caucasian range (Baku, Tiflis, Gouria, Kouban, Taman, Groznoe, Dagestan), I developed in 1876 the hypothesis of the mineral origin of naphtha expounded further on. Berthelot even made a suggestion of the same kind, and in recent times Moissan holds

more probably its formation may be attributed to the action of water penetrating through the crevasses formed on the mountain slopes and reaching to the heart of the earth, to that kernel of heated metallic matter which must be accepted as existing in the interior of the earth. And as meteoric iron often contains carbon (like cast iron), so, accepting the existence of such carburetted iron at unattainable depths in the interior of the earth, it may be supposed that naphtha was produced by the action of water penetrating through the crevices of the strata during the upheaval of mountain chains,⁵⁷ because

the same opinion, although there are yet many men of science who ascribe the origin of naphtha to the antediluvian remains of the animal and vegetable world.

⁵⁷ During the upheaval of mountain ranges, crevasses would be formed at the peaks with openings upwards, and at the foot of the mountains with openings downwards. These cracks in course of time fill up, but the younger the mountains the fresher the cracks (the Alleghany Mountains are, without doubt, more ancient than the Caucasian, which were formed during the Tertiary epoch); through them water must gain access deep into the recesses of the earth to an extent that could not occur on the level (on plains). The situation of naphtha at the foot of mountain chains is the principal argument in the following hypothesis.

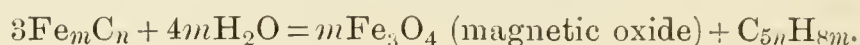
Another fundamental reason is the consideration of the mean density of the earth. Cavendish, Airy, Cornu, Boys, and many others who have investigated the subject by various methods, found that, taking water as 1, the mean density of the earth is nearly 5.5. As at the surface, water and all rocks (sand, clay, limestone, granite, &c.) have a density less than 3, it is evident (as solid substances are but slightly compressible even under the greatest pressure) that inside the earth there are substances of a greater density—indeed, not less than 7 or 8. What conclusion, then, can be arrived at? Anything heavy contained in the bosom of the earth must be distributed not only on its surface, but throughout the whole solar system, for everything tends to show that the sun and planets are formed from the same material, and according to the hypothesis of Laplace and Kant it is most probable, and indeed must necessarily be held, that the earth and planets are but fragments of the solar atmosphere, which have had time to cool considerably and become masses semi-liquid inside and solid outside, forming both planets and satellites. The sun amongst other heavy elements contains a great deal of iron, as is shown by spectrum analysis. There is also much of it in an oxidised condition on the surface of the earth. Meteoric stones, carried as fragmentary planets in the solar system and sometimes falling upon the earth, consisting of siliceous rocks similar to terrestrial ones, often contain either dense masses of iron (for example, the Pallosovo iron preserved in the St. Petersburg Academy of Sciences) or granular masses (for instance, the Okhansk meteorite of 1886). It is therefore possible that the interior of the earth contains much iron in a metallic state. This might be anticipated from the hypothesis of Laplace, for the iron must have been compressed into a liquid at that period when the other component parts of the earth were still strongly heated, and oxides of iron could not then have been formed. The iron was covered with slags (mixtures of silicates like glass fused with rocky matter) which did not allow it to burn at the expense of the oxygen of the atmosphere or of water, just at that time when the temperature of the earth was very high. Carbon was in the same state; its oxides were also capable of dissociation (Deville); it is also but slightly volatile, and has an affinity for iron, and iron carbide is found in meteoric stones (as also are carbon and even the diamond). Thus the supposition of the existence of iron carbides in the interior of the earth was derived by me from many indications, which are to some extent confirmed by the fact that granular pieces of iron have been found in some basalts (ancient lava) as well as in meteoric stones. The occurrence of iron in contact with carbon during the formation of

water with iron carbide should give iron oxide and hydrocarbons.⁵⁸ Direct experiment (Cloëz, Mendeléeff) proves that the so-called *Spiegel-eisen* (manganiferous iron, rich in chemically combined carbon), when treated with acids, gives liquid hydrocarbons⁵⁹ which in composition, appearance, and properties are completely identical with naphtha,⁶⁰ and

the earth is all the more probable because those elements predominate in nature which have small atomic weights, and among them the most widely diffused, the most difficultly fusible, and therefore the most easily condensed (Chapter XV.), are carbon and iron. They passed into the liquid state when all compounds were at a temperature of dissociation.

The reaction of the iron and carbon would give carbide of iron, which would remain in an incandescent state inside the earth. And the action of water, especially salt-water, on this carbide of iron can give naphtha, C_nH_{2n} .

⁵⁸ The following is the typical equation for this formation :



⁵⁹ Cloëz investigated the hydrocarbons formed when cast iron is dissolved in hydrochloric acid, and found C_nH_{2n} and others. I treated crystalline manganiferous cast iron with the same acid, and obtained a liquid mixture of hydrocarbons exactly similar to natural naphtha in taste, smell, and reaction.

⁶⁰ Naphtha was probably produced during the upheaval of all mountain chains, but only in some cases were the conditions favourable to its being preserved underground. The water penetrating below formed there a mixture of naphtha and aqueous vapours, and this mixture issued through fissures to the cold parts of the earth's crust. The naphtha vapours, on condensing, formed naphtha, which, if there were no obstacles, appeared on the surface of land and water. Here part of it soaked through formations (possibly the bituminous slates, schists, dolomites, &c., were thus formed), another part was carried away on the water, became oxidised, evaporated, and was driven to the shores (the Caucasian naphtha probably in this way, during the existence of the Aralo-Caspian sea, was carried as far as the Sisran banks of the Volga, where many strata are impregnated with naphtha and products of its oxidation resembling asphalt and pitch); a great part of it was burnt in one way or another—that is, gave carbonic anhydride and water. If the mixture of vapours, water, and naphtha formed inside the earth had no free outlet to the surface, it nevertheless would find its way through fissures to the superior and colder strata, and there become condensed. Some of the formations (clays) which do not absorb naphtha were only washed away by the warm water, and formed mud, which we also now observe issuing from the earth in the form of mud volcanoes. The neighbourhood of Baku and the whole of the Caucasus near the naphtha districts are full of such volcanoes, which from time to time are in a state of eruption. In old naphtha beds (such as the Pensylvanian) even these blow-holes are closed, and the mud volcanoes have had time to be washed away. The naphtha and the gaseous hydrocarbons formed with it, under the pressure of the overlying earth and water, impregnated the layers of sand, which are capable of absorbing a great quantity of such liquid, and if above this there were strata impermeable to naphtha (dense, clayey, damp strata) the naphtha would accumulate in them. It is thus preserved from remote geological periods up to the present day, compressed and dissolved under the pressure of the gases which burst out in places forming naphtha fountains. If this be granted, it may be thought that in the comparatively new (geologically speaking) mountain chains, such as the Caucasian, naphtha is even now being formed. Such a supposition may explain the remarkable fact that, in Pennsylvania, localities where naphtha had been rapidly worked for five years, have become exhausted, and it becomes constantly necessary to have recourse to sinking new wells in fresh places. Thus, from the year 1859, the workings were gradually transferred along a line running parallel to the Alleghany Mountains for a distance of more than 200 miles; they are now almost exhausted, and have been trans-

carbide of uranium forms them directly when acted on by water (Moissan).

ferred to Ohio and Texas. In Baku the industry dates from time immemorial (the Persians worked near the village of Ballaghana), and up to the present time keeps to one and the same place. The amounts of the Pennsylvanian and Baku annual outputs are at present equal—namely, about 500 million poods (eight million tons). It may be that the Baku beds, as being of more recent geological formation, are not so exhausted by nature as those of Pennsylvania, and perhaps in the neighbourhood of Baku naphtha is still being formed, as is partially indicated by the continued activity of the mud volcanoes. However, the bearings have also become deeper at Baku in the course of years; thus in the eighties the depth was about 80 fathoms, and in 1902 it had increased to 150 fathoms.

As many varieties of naphtha contain in solution solid slightly volatile hydrocarbons like paraffin and mineral wax, the production of ozokerite, or mountain wax, is accounted for as accompanying that of naphtha. Ozokerite is found in Galicia, also in the neighbourhood of Novorossisk, in the Caucasus, and on the islands of the Caspian Sea (particularly in the Chileken and Holy Islands); it is met with in large masses, and is used for the production of paraffin and *ceresine*, for the manufacture of candles, and similar purposes.

As the naphtha treasures of the Caucasus have hardly been exploited (near Baku and near Kouban and Grosnyi), and as naphtha finds numerous uses, the subject presents most interesting features to chemists and geologists, and is worthy of the close attention of practical men.

CHAPTER IX

COMPOUNDS OF CARBON WITH OXYGEN AND NITROGEN

CARBONIC ANHYDRIDE (or carbonic acid or carbon dioxide, CO_2) was the first of all gases to be distinguished from atmospheric air. Paracelsus and van Helmont, in the sixteenth century, knew that on heating limestone a peculiar gas separated, which is also formed during the alcoholic fermentation of saccharine solutions (for instance, in the manufacture of wine); they knew that it was identical with the gas which is produced by the combustion of charcoal, and that in some

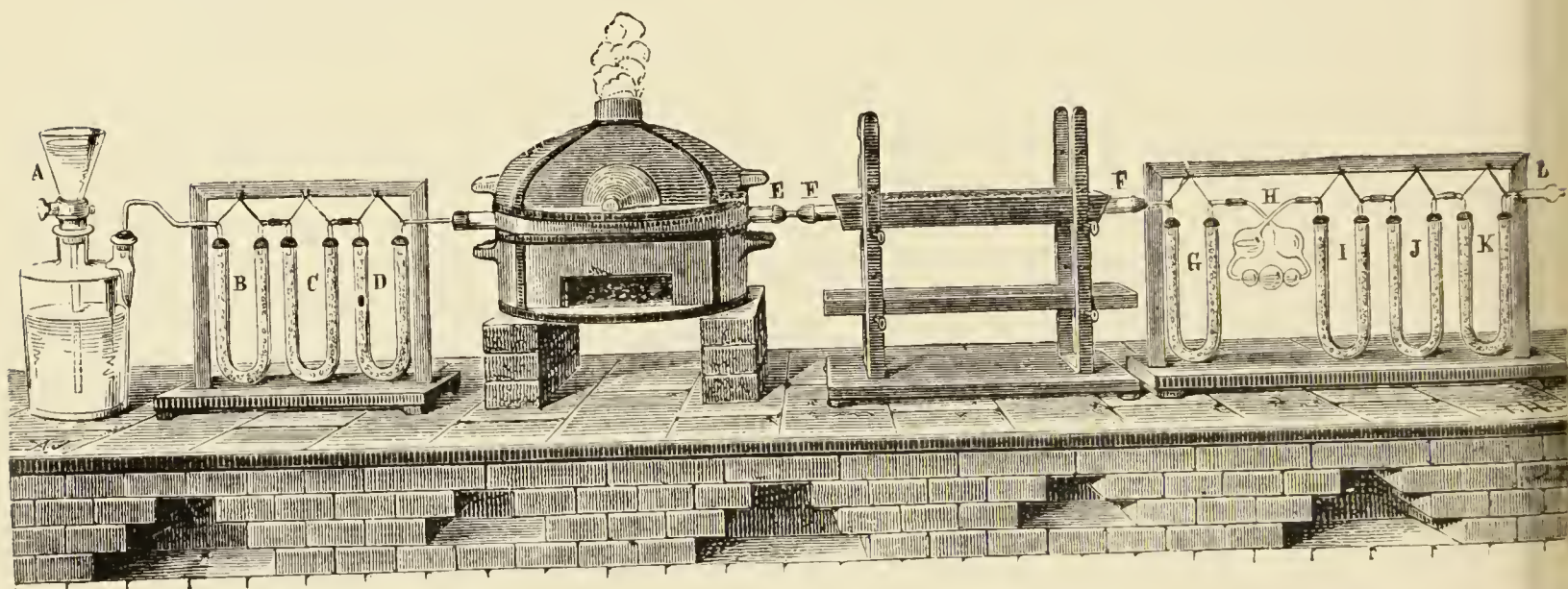


FIG. 70.—Dumas and Stas' apparatus for determining the composition of carbonic anhydride. Carbon, graphite, or a diamond is placed in the tube E in the furnace, and heated in a stream of oxygen displaced from the bottle by water flowing from A. The oxygen is purified from carbonic anhydride and water in the tubes B, C, D. Carbonic anhydride, together with a certain amount of carbon monoxide, is formed in E. The latter is converted into carbonic acid by passing the products of combustion through a tube, F, containing cupric oxide heated in a furnace. The cupric oxide oxidises this CO into CO_2 , forming metallic copper. The potash bulbs H and tubes I, J, K retain the carbonic anhydride. Thus, knowing the weight of carbon taken and the weight of the resultant carbonic anhydride (by weighing H, I, J, K before and after the experiment), the composition of carbonic anhydride and the equivalent of carbon may be determined.

cases it is found in nature. In course of time it was found that this gas is absorbed by alkali, forming a salt which, under the action of acid, again yields this same gas. Priestley found that this gas exists in air, and Lavoisier determined its formation during respiration, combustion, putrefaction, and during the reduction of the oxides of metals by charcoal; he determined its composition, and showed that it contains only oxygen and carbon. Berzelius, Dumas with Stas, and

Roscoe determined its composition, showing that it contains twelve parts of carbon to thirty-two of oxygen. The composition by volume of this gas is determined from the fact that during the combustion of charcoal in oxygen, the volume remains unchanged; that is to say, **carbonic anhydride occupies the same volume as the oxygen which it contains**—the atoms of the carbon being, so to speak, squeezed in between the atoms of the oxygen. O_2 occupies two volumes and is a molecule of ordinary oxygen; CO_2 likewise occupies two volumes, and expresses the composition and molecular weight of the gas. The relation between hydrogen, H_2 , and acetylene, C_2H_2 , is the same, only in that case we have C_2 , and here one atom of carbon.

Carbonic anhydride exists **in nature**, both in a free state and in the most varied compounds. In a free state it is always contained (Chap. V.) in the air, and in solution exists in all kinds of water. It is evolved from volcanoes, from mountain fissures, and in some caves. The well-known Dog grotto, near Agnano on the bay of Baiæ, near Naples, furnishes the best known example of such an evolution. Similar sources of carbonic anhydride are also found in other places. In France, for instance, there is a well-known poisonous fountain in Auvergne. It is a round hole, surrounded with luxurious vegetation and constantly evolving carbonic anhydride. In the woods surrounding the Lacher Lake near the Rhine, in the neighbourhood of extinct volcanoes, there is a depression constantly filled with this same gas. The insects which fly to this place perish, animals being unable to breathe the gas. The birds chasing the insects also die, and this is turned to profit by the local peasantry. Many mineral springs carry into the air enormous quantities of this gas. Vichy in France, Sprüdel in Germany, and Narzan in Russia (in Kislovodsk near Piatigorsk) are known for their carbonated gaseous waters. Much of this gas is also evolved in mines, cellars, diggings, and wells. People descending into such places are suffocated. The combustion, putrefaction, and fermentation of organic substances give rise to the formation of carbonic anhydride. It is also introduced into the atmosphere during the respiration of animals at all times and during the respiration of plants in darkness and also during their growth. Very simple experiments prove the formation of carbonic anhydride under these circumstances; thus, for example, if the air expelled from the lungs be passed through a glass tube into a transparent solution of lime (or baryta) in water a white precipitate will soon be formed consisting of an insoluble compound of lime and carbonic anhydride. By allowing the seeds of plants to grow under a bell-jar, or in a closed vessel, the formation of carbonic anhydride may be similarly confirmed. By confining an animal, a mouse, for

instance, under a bell-jar, the quantity of carbonic acid which it evolves may be exactly determined, and it will be found to be many grams per day for a mouse. Such experiments on the **respiration of animals** have also been made with great exactitude with large animals, such as men, bulls, sheep, &c. By means of enormous hermetically closed bell-receivers and the analysis of the gases evolved during respiration it was found that a man expels about 900 grams (more than two pounds) of carbonic anhydride per diem, and absorbs during this time 700 grams of oxygen.¹ It must be remarked that the carbonic anhydride of the air constitutes the fundamental food of plants (Chapters III., V., and VIII.). Carbonic anhydride in a state of combination with a variety of other substances is perhaps even more widely distributed in nature than in a free state.^{1a} Some of these substances are very stable and form a

¹ The quantity of carbonic acid gas exhaled by a man during the twenty-four hours is not produced uniformly; during the night more oxygen is taken in than during the day (by night, in twelve hours, about 450 grams), and more carbonic anhydride is separated by day than during night-time and repose; thus, of the 900 grams produced during the twenty-four hours about 375 are given out during the night and 525 by day. This depends on the formation of carbonic anhydride during the work performed by the man in the day. Every movement is the result of some change of matter, for force cannot be self-created (in accordance with the law of the conservation of energy). Proportionally to the amount of carbon consumed an amount of energy is stored up in the organism and is consumed in the various movements performed by animals. This is proved by the fact that during work a man exhales 900 grams of carbonic anhydride in twelve hours instead of 525, absorbing the same amount of oxygen as before. The man, as it were, burns. After a working day a man exhales by night almost the same amount of carbonic anhydride as after a day of rest, so that during a total twenty-four hours a man exhales about 1,300 grams of carbonic anhydride and absorbs about 950 grams of oxygen. So that during work the change of matter increases. The carbon expended on the work is obtained from the food; on this account the food of animals ought certainly to contain carbonaceous substances capable of dissolving under the action of the digestive fluids, and of passing into the blood, or, in other words, capable of being digested. Such food for man and all other animals is formed of vegetable matter, or of parts of other animals. The latter in every case obtain their carbonaceous matter from plants, in which it is formed by the separation of the carbon from the carbonic anhydride taken up during the day by the respiration of the plants. The volume of the oxygen exhaled by plants is almost equal to the volume of the carbonic anhydride absorbed; that is to say, nearly all the oxygen entering into the plant in the form of carbonic anhydride is liberated in a free state, whilst the carbon from the carbonic anhydride remains in the plant. At the same time the plant absorbs moisture by its leaves and roots. By a process which is unknown to us, this absorbed moisture and the carbon obtained from the carbonic anhydride enter into the composition of the plants in the form of so-called *carbohydrates*, composing the greater part of the vegetable tissues, starch and cellulose of the composition $C_6H_{10}O_5$ being representatives of them. They may be considered, like all carbohydrates, as compounds of carbon and water, $6C + 5H_2O$. In this way a **circulation** of the carbon in nature goes on by means of vegetable and animal organisms, in which changes the principal factor is the carbonic anhydride of the air.

^{1a} Hence, and from the fact that coal is derived from plants which were nourished by CO_2 , it follows that the amount of CO_2 in the air in former geological periods was greater than now. This would also affect the diathermancy of the atmosphere and the climate of the globe (see Chap. V., note 25)

large portion of the earth's crust. For instance, limestones, calcium carbonate, CaCO_3 , were formed as precipitates in the seas formerly existing on the earth; this is proved by their stratified structure and the number of remains of sea animals which they frequently contain. Chalk, lithographic stone, limestone, marls (a mixture of limestone and clay), and many other rocks are examples of such carboniferous sedimentary formations. Carbonates with various other bases—such as, for instance, magnesia, ferrous oxide, zinc oxide, &c.—are often found in nature. The shells of molluscs also have the composition CaCO_3 , and many limestones were exclusively formed from the shells of minute organisms. As carbonic anhydride (together with water) is produced during the combustion of all organic compounds in a stream of oxygen or by heating them with substances which readily part with their

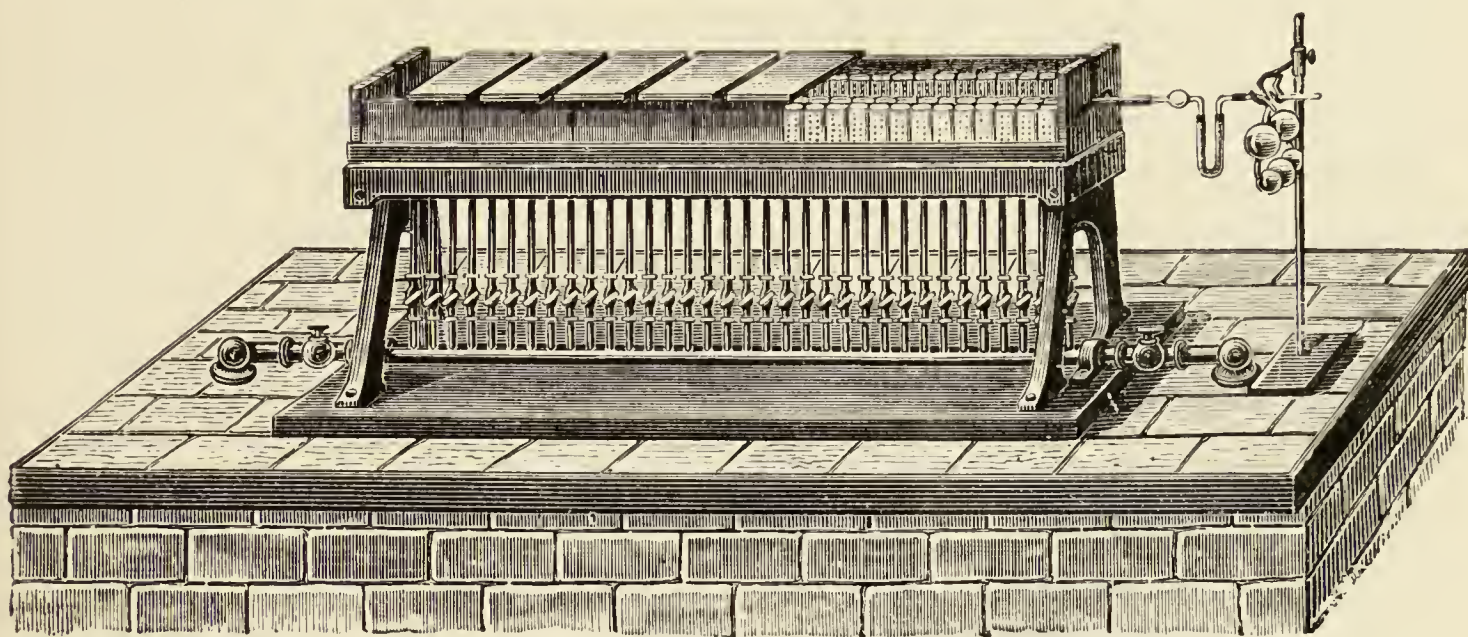


FIG. 71.—Apparatus for the combustion of organic substances by igniting them with oxide of copper.

oxygen—for instance, with copper oxide—this method is employed for estimating the amount of carbon in organic compounds, more especially as the CO_2 can be easily collected and the amount of carbon calculated from its weight. As a rule, for this purpose a hard glass tube, closed at one end, is filled with a mixture of the organic substance (about 0.2 gram) and copper oxide. The open end of the tube is fitted with a cork and tube containing calcium chloride for absorbing the water formed by the oxidation of the substance. This tube is hermetically connected (by a caoutchouc tube) with potash bulbs or other weighing apparatus (Chapter V.) containing alkali destined to absorb the carbonic anhydride. The increase in weight of this apparatus shows the amount of carbonic anhydride formed during the combustion of the given substance, and the quantity of carbon may be determined from this, because three parts of carbon give eleven parts of carbonic anhydride.

For the preparation of carbonic anhydride in laboratories and often in manufactories, either charcoal is simply burnt or more frequently various kinds of native calcium carbonate are used, being treated with some acid; it is most usual to employ the so-called muriatic acid—that is, an aqueous solution of hydrochloric acid, HCl —because the substance formed, calcium chloride, CaCl_2 , is soluble in water and does not hinder the further action of the acid on the calcium carbonate (sulphuric acid gives insoluble gypsum). For calcium carbonate, either limestone, chalk, or marble is used: ² $\text{CaCO}_3 + 2\text{HCl} = \text{CaCl}_2 + \text{H}_2\text{O} + \text{CO}_2$. The nature of the reaction in this case is the same as in the decomposition of nitre by sulphuric acid; only in the latter case a hydrate is formed, and in the former an anhydride of the acid, because the hydrate, carbonic acid, H_2CO_3 , is unstable, and as soon as it separates decomposes into water and its own anhydride. It is evident from the explanation of the cause of the action of sulphuric acid on nitre that not every acid can be employed for obtaining carbonic anhydride, for those will not set it free which are chemically but slightly energetic, or are insoluble in water, or are themselves as volatile as carbonic anhydride.³ But as many acids are soluble in water and are less volatile than carbonic anhydride, the latter is evolved by the

² If porous limestone—for instance, chalk—be treated with sulphuric acid diluted with an equal volume of water, the liquid is absorbed and acts on the mass of the salt, the evolution of carbonic anhydride continuing evenly for a long time. Instead of calcium carbonate other carbonates may of course be used; for instance, washing-soda, Na_2CO_3 , which is often chosen when it is required to produce a rapid stream of carbonic anhydride (for example, for liquefying it). But natural crystalline magnesium carbonate is with difficulty decomposed by hydrochloric and sulphuric acids. When for manufacturing purposes—for instance, in precipitating lime in sugar-works—a large quantity of carbonic acid gas is required, it is generally obtained by burning charcoal, and the products of combustion, rich in carbonic anhydride, are forced into the liquid containing the lime, and the carbonic anhydride is thus absorbed. Another method which consists in using the carbonic anhydride separated during fermentation, or that evolved from limekilns, is also practised. During the fermentation of sweet-wort, grape-juice, and other similar saccharine solutions, the glucose, $\text{C}_6\text{H}_{12}\text{O}_6$, changes under the influence of the yeast organism, forming alcohol ($2\text{C}_2\text{H}_6\text{O}$), and carbonic anhydride (2CO_2) which separates in the form of gas; if the fermentation proceeds in closed bottles sparkling wine is obtained. When carbonic acid gas is prepared for saturating water and other beverages it is necessary to use it in a pure state; whilst when evolved from ordinary limestone by the aid of acids it contains, besides a certain quantity of acid, the organic matters of the limestone. In order to diminish the quantity of these substances the densest kinds of dolomites are used, which contain less organic matter, and the gas formed is passed through various washing apparatus, and then through a solution of potassium permanganate, which absorbs organic matter and does not take up carbonic anhydride.

³ Hypochlorous acid, HClO , and its anhydride, Cl_2O , do not displace carbonic acid, and hydrogen sulphide has the same relation to carbonic acid as nitric acid to hydrochloric—an excess of either one displaces the other.

action of most acids on its salts, and this reaction takes place at ordinary temperatures.⁴

For the preparation of carbonic anhydride in laboratories, marble is generally used. It is placed in a Woulfe's bottle and treated with hydrochloric acid in an apparatus similar to the one used for the production of hydrogen. The gas evolved carries away through the tube part of the volatile hydrochloric acid, and it is therefore necessary to wash the gas by passing it through another Woulfe's bottle containing water.⁵

Carbonic anhydride may also be prepared by heating many of the salts of carbonic acid; for instance, by heating magnesium carbonate, MgCO_3 (e.g., in the form of dolomite), the separation is easily effected, particularly in the presence of the vapours of water. The acid salts of carbonic acid (for instance, NaHCO_3 , see further on) readily and abundantly give carbonic anhydride when heated.

Carbonic anhydride is colourless, has a slight smell and a faint acid taste; its density in a gaseous state is twenty-two times as great as that of hydrogen, because its molecular weight is forty-four.⁶

⁴ Thus, in preparing the ordinary effervescing powders, sodium bicarbonate (or acid carbonate of soda) is used, and is mixed with powdered citric or tartaric acid. In a dry state these powders do not evolve carbonic anhydride, but when mixed with water the evolution takes place briskly, owing to the substances passing into solution. The salts of carbonic acid may be recognised from the fact that they evolve carbonic acid with a hissing noise when treated with acids. If vinegar, which contains acetic acid, be poured upon limestone, marble, malachite (containing copper carbonate), &c., carbonic anhydride is evolved with a hissing noise. It is noteworthy that neither hydrochloric acid, nor even sulphuric acid, nor acetic acid acts on limestone except in presence of water. We shall refer to this later on.

⁵ The direct observations made (1876) by Messrs. Bogouski and Kayander lead to the conclusion that the quantity of carbonic anhydride evolved by the action of acids on marble (as homogeneous as possible) is directly proportional to the time of action, the extent of surface, and the degree of concentration of the acid, and inversely proportional to the molecular weight of the acid. If the surface of a piece of Carrara marble be equal to one decimetre, the time of action one minute, and one cubic decimetre or litre of the acid contains one gram of hydrochloric acid, then about 0.02 gram of carbonic anhydride will be evolved. If the litre contains n grams of hydrochloric acid, then by experiment the amount will be $n \times 0.02$ of carbonic anhydride. Therefore, if the litre contains 36.5 (= HCl) grams, about 0.73 gram of carbonic anhydride (about half a litre) would be evolved per minute. If nitric acid or hydrobromic acid be used instead of hydrochloric, then, with a combining proportion of the acid, the same quantity of carbonic anhydride will be evolved; thus, if the litre contains 63 (= HNO_3) grams of nitric acid, or 81 (= HBr) grams of hydrobromic acid, the quantity of carbonic anhydride evolved will still be 0.73 gram. Spring (in 1890) made a series of similar determinations.

⁶ As carbonic anhydride is one and a half time **heavier than air**, it diffuses with difficulty, and therefore does not easily mix with air, but sinks in it. This may be shown in various ways; for instance, the gas may be carefully poured from one vessel into another containing air. If a lighted taper be plunged into the vessel containing carbonic anhydride it is extinguished, and then, after pouring the gas into the other cylinder, it will burn in the former and be extinguished in the latter. If a certain quantity of carbonic anhydride be poured into a vessel containing air, and soap-bubbles be introduced, they will only sink as far as the stratum where the atmosphere of carbonic anhydride commences,

It is an example of those gaseous substances which have been long ago transformed into all the three states. In order to obtain **liquid** carbonic anhydride, the gas must be submitted to a pressure of thirty-six atmospheres at 0° .⁷ Its absolute boiling-point (critical temperature) is $+32^{\circ}$.⁸ Liquid carbonic anhydride is colourless and does not mix with water, but it is soluble in alcohol, ether, and oils; at 0° its specific gravity is 0.9.^{8a} The boiling-point of this liquid lies at -78° ; that is to say, the pressure of carbonic acid gas at that temperature is nearly that of the atmosphere. At the ordinary pressure liquid CO_2 remains as such for some time, if it does not exceed 50° , on account of its requiring a considerable amount of heat for its evaporation (latent heat at $0^{\circ}=55$ units). If the evaporation takes place rapidly from a considerable surface—for instance, when the liquid is poured in a thin stream—such a fall of temperature occurs that a part of the carbonic anhydride is transformed into a solid snowy mass melting at about -60° . Water, mercury, and many other liquids freeze on coming into contact with carbonic anhydride snow.⁹ In this form carbonic anhydride may be preserved for a long time in the open air, because it requires still more heat to turn it into a gas than when in a liquid state.^{9a}

as this latter is heavier than the soap-bubbles filled with air. Naturally, after a certain lapse of time, the carbonic anhydride will be diffused throughout the vessel, and form a uniform mixture with the air, just as salt in water.

⁷ This liquefaction was first observed by Faraday, who sealed up a mixture of a carbonate and sulphuric acid in a tube. This method was afterwards very considerably improved by Thilorier and Natterer, whose apparatus is described in Chapter VI. in discussing N_2O . It is, however, necessary to remark that the preparation of liquid carbonic anhydride requires good liquefying apparatus, constant cooling, and a rapid preparation of large masses of carbonic anhydride.

⁸ Carbonic anhydride, having the same molecular weight as nitrous oxide, very much resembles it when in a liquid state.

^{8a} When poured into a tube, which is then sealed up, liquefied carbonic anhydride can be easily preserved, because a thick tube easily supports the pressure (about 50 atmospheres) exerted by the liquid at the ordinary temperature. At -20° the sp. gr. is almost = 1, at $+20^{\circ}$ about 0.77, and at the critical temperature, $+31.4^{\circ}$, about 0.46. At this latter temperature gaseous CO_2 has almost the same density, for the pressure is almost 75 atmospheres.

⁹ When a fine stream of liquid carbonic anhydride is discharged into a closed metallic vessel, about one-third of its mass solidifies and the remainder evaporates. In employing solid carbonic anhydride for making experiments at low temperatures, it is best to use it mixed with ether, otherwise there will be few points of contact. If a stream of air be blown through a mixture of liquid carbonic anhydride and ether, the evaporation proceeds rapidly, and great cold is obtained. At present in some special manufactories (and for making artificial mineral waters) carbonic anhydride is liquefied on the large scale, filled into wrought-iron cylinders provided with a valve, and in this manner it can be transported and preserved safely for a long time. It is used, for instance, in breweries.

^{9a} Solid carbonic anhydride (sp. gr. about 1.4), notwithstanding its very low temperature, can be safely placed on the hand, because it continually evolves gas which prevents its coming into actual contact with the skin; but if a piece be squeezed between

Carbonic anhydride as a liquefiable gas **dissolves** with great facility in **water**, alcohol, and other liquids. Its solubility in water has been already spoken of in the first chapter. Carbonic anhydride is still more soluble in alcohol than in water, one volume of alcohol dissolving 4·3 volumes of this gas at 0° and 2·9 volumes at 20°.

Aqueous solutions of carbonic anhydride, under a pressure of several atmospheres, are now prepared artificially, because water saturated with this gas promotes digestion and quenches thirst. For this purpose the carbonic anhydride is pumped by means of a force-pump into a closed vessel containing the liquid and then bottled off, taking special means to ensure rapid and air-tight corking. Various effervescing drinks and artificially effervescing wines are thus prepared. The presence of carbonic anhydride has an important significance in nature, because by its means water acquires the property of decomposing and dissolving many substances which are not acted on by pure water: for instance, calcium phosphates and carbonates are soluble in water containing carbonic acid. If the water in the interior of the earth be saturated with carbonic acid under pressure, the quantity of calcium carbonate in solution may reach three grams per litre, and on issuing at the surface, as the carbonic anhydride escapes, the calcium carbonate will be deposited.¹⁰ Water charged with carbonic anhydride brings about the destruction of many rocky formations by removing the lime, alkali, &c., from them. This process has been going on, and still continues, on an enormous scale. Rocks contain silica and the oxides of various metals; amongst others, the oxides of aluminium, calcium, and sodium. Water charged with

the fingers, it produces a severe frost-bite similar to a burn. If the snowlike solid be mixed with ether, a semi-liquid mass is obtained, which is employed for artificial refrigeration. This mixture may be used for liquefying many other gases—such as chlorine, nitrous oxide, hydrogen sulphide, and others. The evaporation of such a mixture proceeds with far greater rapidity under the receiver of an air-pump, and consequently the refrigeration is more intense.

¹⁰ If such water trickles through crevices and enters a cavern, the evaporation will be slow, and therefore, in those places from which the water drips, growths of calcium carbonate will be formed, just like the icicles formed on the gutters of roofs in winter-time. Such conical and cylindrical stony growths form the so-called stalactites or pendants hanging from above and stalagmites formed on the bottom of caves. Sometimes these two kinds meet together, forming entire columns filling the cave. Many of these caves are remarkable for their picturesqueness; for instance, the cave of Antiparos, in the Grecian Archipelago. This same action also forms spongy masses of calcium carbonate in those places where the springs come to the surface of the earth. It is therefore very evident that a calcareous solution is sometimes capable of penetrating plants and filling the whole of their mass with calcium carbonate. This is one of the forms of petrified plants. Calcium phosphate in solution in water containing carbonic acid plays an important part in the nourishment of plants, because all plants contain both lime and phosphoric acid.

carbonic acid dissolves both the latter, transforming them into carbonates. The waters of the ocean ought, as the evolution of the carbonic anhydride proceeds, to precipitate salts of lime; these are actually found everywhere on the surface of the ground in those places which formerly formed the bed of the ocean. The presence of carbonic anhydride in solution in water is essential to the nourishment and growth of water plants.

Although carbonic anhydride is soluble in water, no definite hydrate is formed;¹¹ nevertheless an idea of the composition of this hydrate may be formed from that of the salts of carbonic acid, because a hydrate is nothing but a salt in which the metal is replaced by hydrogen. As carbonic anhydride forms salts of the composition K_2CO_3 , Na_2CO_3 , $HNaCO_3$, &c., carbonic acid ought to have the composition H_2CO_3 —that is, it ought to contain $CO_2 + H_2O$. Whenever this substance is formed, it decomposes into its component parts—that is, into water and carbonic anhydride. **The acid properties** of carbonic anhydride^{11a} are demonstrated by its being directly absorbed by alkaline solutions, forming salts with them. Unlike nitric, HNO_3 , and similar monobasic acids which with univalent metals (exchanging one atom for one atom of hydrogen) give salts such as those of potassium, sodium, and silver containing only one atom of the metal ($NaNO_3$, $AgNO_3$), and with bivalent¹² metals (such as calcium, barium, lead) salts containing two acid groups—for example, $Ca(NO_3)_2$, $Pb(NO_3)_2$ —carbonic acid, H_2CO_3 , is **dibasic**, that is, contains two atoms of hydrogen in the hydrate or two atoms of univalent metals in its salts: for example, Na_2CO_3 is washing soda, a normal salt; $NaHCO_3$ is the bicarbonate, an acid salt. Therefore, if M' be a univalent metal, its carbonates in general are the normal carbonate M'_2CO_3 and the acid carbonate, $M'HCO_3$; or if M'' be a bivalent metal (replacing H_2) its normal carbonate will be $M''CO_3$; these metals do not usually form

¹¹ The crystallhydrate, $CO_2 \cdot 8H_2O$ of Wroblewski (Chap. I., note 67), is, in the first place, only formed under special conditions; in the second place, its existence still requires confirmation; and in the third place, it does not correspond with that hydrate H_2CO_3 which should occur, judging from the composition of the salts.

^{11a} It is easy to demonstrate the acid properties of carbonic anhydride by taking a long tube, closed at one end, and filling it with this gas; a test-tube is then filled with a solution of an alkali (for instance, sodium hydroxide), which is then poured into the long tube and the open end corked. The solution is then well shaken in the tube, and the corked end plunged into water. If the cork be now withdrawn under water, the water will fill the tube. The vacuum obtained by the absorption of the carbonic anhydride by an alkali is so complete that even an electric discharge will not pass through it. This method is often applied to produce a vacuum.

¹² The reasons for distinguishing the uni-, bi-, tri-, and quadri-valent metals will be explained hereafter on passing from the univalent metals (Na , K , Li) to the bivalent ones (Mg , Ca , Ba), Chap. XIV.

acid salts in a free state, as we shall see further on. The dibasic character of carbonic acid is akin to that of sulphuric acid, H_2SO_4 ,¹³ but the latter, in distinction from the former, is an example of the energetic or strong acids (such as nitric or hydrochloric), whilst in carbonic acid we observe but feeble development of the acid properties; hence carbonic acid must be considered to be a **weak acid**. This conception must, however, be taken as only comparative.¹⁴ The feeble

¹³ Up to the year 1840, or thereabout, acids were not distinguished by their basicity. Graham, while studying phosphoric acid, H_3PO_4 , and Liebig, while studying many organic acids, distinguished mono-, di-, and tri-basic acids. Gerhardt and Laurent generalised these relations, showing that this distinction extends over many reactions (for instance, to the faculty of dibasic acids of forming neutral and acid salts with alkalies, KHO or NaHO , or with alcohols, RHO , &c.); but now, since a definite conception as to atoms and molecules has been arrived at, *the basicity of an acid is determined by the number of hydrogen atoms, contained in a molecule of the acid, which can be exchanged for metals*. If carbonic acid forms acid salts, NaHCO_3 , and normal salts, Na_2CO_3 , it is evident that the hydrate is H_2CO_3 , a dibasic acid. Otherwise it is at present impossible to account for the composition of these salts. But when $\text{C} = 6$ and $\text{O} = 8$ were taken, then the formula CO_2 expressed the composition, but not the molecular weight, of carbonic anhydride; and the composition of the normal salt would be $\text{Na}_2\text{C}_2\text{O}_6$, or NaCO_3 , so that carbonic acid might have been regarded as a monobasic acid. The acid salt would then have been represented by $\text{NaCO}_3, \text{HCO}_3$. Such questions were the cause of much argument and difference of opinion among chemists about forty years ago. At present there cannot be two opinions on the subject, if the law of Avogadro-Gerhardt and its consequences be strictly adhered to. It may, however, be observed here that the monobasic acids R(OH) were for a long time considered to be incapable of being decomposed into water and anhydride, and this property was ascribed to the dibasic acids R(OH)_2 as containing the elements necessary for the separation of the molecule of water, H_2O . Thus H_2SO_4 or $\text{SO}_2(\text{OH})_2$, H_2CO_3 , or CO(OH)_2 , and other dibasic acids decompose into an anhydride, RO , and water, H_2O . But as nitrous, HNO_2 , iodic, HIO_3 , hypochlorous, HClO , and other monobasic acids easily give their anhydrides N_2O_3 , I_2O_5 , Cl_2O , &c., that method of distinguishing the basicity of acids, although it fairly well satisfies the requirements of organic chemistry, cannot be considered correct. It may also be remarked that up to the present time not one of the dibasic acids has been found to have the faculty of being distilled without being decomposed into anhydride and water (even H_2SO_4 , on being evaporated and distilled, gives $\text{SO}_3 + \text{H}_2\text{O}$), and the decomposition of acids into water and anhydride proceeds particularly easily with feebly energetic acids, such as carbonic, nitrous, boric, and hypochlorous. Let us add that carbonic acid, as a hydrate corresponding to marsh gas, $\text{C(HO)}_4 = \text{CO}_2 + 2\text{H}_2\text{O}$, ought to be tetrabasic. But in general it does not form such salts. Basic salts, however, such as $\text{CuCO}_3, \text{CuO}$, may be regarded in this sense, for CCu_2O_4 corresponds with CH_4O_4 , since Cu corresponds with H_2 . Amongst the ethereal salts (alcoholic derivatives) of carbonic acid corresponding cases are, however, observed; for instance, ethylic orthocarbonate, $\text{C(C}_2\text{H}_5\text{O)}_4$ (obtained by the action of chloropicrin, $\text{C(NO}_2\text{)Cl}_3$, on sodium ethoxide, $\text{C}_2\text{H}_5\text{ONa}$; boiling-point 158° ; specific gravity, 0.92). The name *orthocarbonic acid* for CH_4O_4 is taken from *orthophosphoric acid*, PH_3O_4 , which corresponds with PH_3 (see Chap. XIX.).

¹⁴ Long ago endeavours were made to find a *measure of the affinity* of acids and bases, because some of the acids, such as sulphuric or nitric, form comparatively stable salts, decomposed with difficulty by heat and water, whilst others, like carbonic and hypochlorous acids, do not combine with feeble bases, and with most of the other bases form salts which are easily decomposed. The same may be said with regard to bases, among which those of potassium, K_2O , sodium, Na_2O , and barium, BaO , may serve as examples of the most powerful, because they combine with the most feeble acids and form a number of salts of

acid properties of carbonic acid may, however, be judged from the *joint evidence* of many properties. With such energetic alkalies as soda and great stability, whilst as examples of the feeblest bases alumina, Al_2O_3 , or bismuth oxide, Bi_2O_3 , may be taken, because these form salts easily decomposed by water or heat if the acid be volatile. Efforts have long since been made to endow the conception of the relative affinity of acids and bases with a measurable degree of exactitude. The most varied methods have been employed for this purpose, and we shall become acquainted with some of them in the following chapter. A wider acquaintance with all these methods must be looked for in works on physical and theoretical chemistry, as the matter cannot yet be considered as fully explained and it comprises much which relates more closely to the province of those physico-chemical phenomena which are of such vital interest at the present time. For my part I think that neither the thermo-chemical investigation of aqueous solutions, nor the changes in volume (see Chap. X., note 27) which take place in the mixing together of solutions of acids and bases, nor the determination of the electro-conductivity of dilute solutions, nor the study of 'distribution,' nor many others of the methods used for determining the measure of the affinity of bases and acids in their solutions, are exempt from the radical defect of neglecting from their consideration the water serving for the solution and having its own chemical reaction on the original and resultant substances. The determination of the so-called 'rate of reaction,' which seems best fitted to give trustworthy results directly related to affinity, is unfortunately not directly applicable to the reaction of acids with bases, as these reactions proceed exceedingly rapidly, although the reaction of alcohols with acids, for instance, proceeds so slowly that the rate can be easily measured. The fact that such acids as HCl , HNO_3 and H_2SO_4 react with far greater rapidity than acetic and formic acids, &c., already shows that the former are more energetic than the latter, but still it seems to me that the measure of 'affinity' cannot in general be identified in this case with the measure of 'time.' Nevertheless the numerous observations made during the nineties, especially in the laboratory of Prof. Ostwald, on these subjects have not only given a vast store of experimental data to science, but also deserve our best attention from a theoretical point of view owing more especially to the fact that the numerical data obtained by various methods are found to be in close agreement. From the following table it is evident that the relations between the so-called molecular electrical conductivity (I) of dilute solutions of different acids coincide with those in which these acids stand as regards distribution (II), and also with the relations existing between their velocities of reaction (III), measured, for example, by the rate of decomposition of methyl acetate (into acid and alcohol) or by the rate of the so-called inversion of cane-sugar, i.e., its transformation into dextrose and levulose; the energy of hydrochloric acid is taken as equal to 100:—

			I.	II.	III.
Hydrochloric acid,	HCl	. .	100	100	100
Hydrobromic acid,	HBr	. .	101	89	105
Nitric acid,	HNO_3	. .	100	100	96
Sulphuric acid,	H_2SO_4	. .	65	49	74
Formic acid,	CH_2O_2	. .	2	4	1
Acetic acid,	$\text{C}_2\text{H}_4\text{O}_2$. .	1	2	1
Oxalic acid,	$\text{C}_2\text{H}_2\text{O}_4$. .	20	24	18
Phosphoric acid,	PH_3O_4	. .	7	—	6

The coincidence of these figures, obtained by so many various methods, indicates a most important and instructive relation between phenomena of different kinds, but in my opinion it does not permit us to assert that the degree of affinity existing between bases and various acids is determined by all these various methods, because the influence of the water must be taken into consideration. On this account, until the theory of solution is more thoroughly worked out, these coincidences (which for the present ought to be treated of in special treatises on chemical mechanics) must be received with great caution.

potash, carbonic acid forms normal salts, soluble in water, but having an alkaline reaction and in many cases themselves acting as alkalies.¹⁵ Only the acid salts of these energetic alkalies, NaHCO_3 and KHCO_3 , have a neutral reaction on litmus, although they, like acids, contain hydrogen, which may be exchanged for metals. The acid salts of such acids as, for instance, sulphuric acid— NaHSO_4 —have a clearly defined acid reaction, and therefore carbonic acid is unable to neutralise the powerful basic properties of such alkalies as potash or soda. Carbonic acid does not even combine at all with feeble bases, such as alumina, Al_2O_3 , so that, if a strong solution of sodium carbonate, Na_2CO_3 , be added to a strong solution of aluminium sulphate, $\text{Al}_2(\text{SO}_4)_3$, instead of aluminium carbonate, $\text{Al}_2(\text{CO}_3)_3$, being formed, carbonic acid separates, for this salt splits up in the presence of water into aluminium hydroxide and carbonic anhydride: $\text{Al}_2(\text{CO}_3)_3 + 3\text{H}_2\text{O} = \text{Al}_2(\text{OH})_6 + 3\text{CO}_2$. Thus feeble bases are unable to retain carbonic acid even at ordinary temperatures. For the same reason, in the case of bases of medium energy, although they form carbonates, the latter are comparatively easily decomposed by heating, as is shown by the decomposition of copper carbonate, CuCO_3 (see Introduction), and even of calcium carbonate, CaCO_3 . Only the normal (not the acid) salts of such powerful bases as potassium and sodium are capable of withstanding a red heat without decomposition. The acid salts—for instance, NaHCO_3 —decompose even on heating their solutions ($2\text{NaHCO}_3 = \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} + \text{CO}_2$), evolving carbonic anhydride. The amount of heat given out by the combination of carbonic acid with bases also shows its feeble acid properties, being considerably less than with energetic acids. Thus if a weak solution of forty grams of sodium hydroxide be saturated (up to the formation of a normal salt) with sulphuric or nitric acid or another powerful acid, from thirteen to fifteen thousand calories are given out, but with carbonic acid the heat evolution is only about ten thousand calories.¹⁶

¹⁵ Thus, for instance, in the washing of fabrics the caustic alkalies, such as sodium hydroxide, in weak solutions, act in removing the fatty matter just in the same way as carbonate solutions, for instance, a solution of soda crystals, Na_2CO_3 . Soap acts in the same way, being composed of feeble acids, either fatty or resinous, combined with alkali. On this account all such substances are applied in manufacturing processes, and answer equally well in practice for bleaching and washing fabrics. Soda crystals or soap are preferred to caustic alkali, because an excess of the latter may have a destructive effect on the fabrics. It may be supposed that in aqueous solutions of soap or soda crystals, part of the base forms caustic alkali; that is to say, the water will compete with the weak acids, and the alkali will be distributed between the latter and the water.

¹⁶ Although carbonic acid is reckoned among the feeble acids, yet there are evidently many others still feebler—for instance, prussic acid, hypochlorous acid, many organic acids, &c. Bases like alumina, or such feeble acids as silica, when in combination with alkalies, are decomposed in aqueous solutions by carbonic acid, but on fusion—that is, without the presence of water—they displace it, clearly showing how much depends,

The majority of carbonates are insoluble in water, and therefore such soluble ones as sodium, potassium, and ammonium carbonates form, in solutions of most other salts, MX or $M''X_2$, insoluble precipitates of the carbonates, M_2CO_3 or $M''CO_3$. Thus, a solution of barium chloride gives with sodium carbonate a precipitate of barium carbonate, $BaCO_3$. For this reason rocks, especially those of aqueous origin, very often contain carbonates; for example, calcium, ferrous, magnesium carbonates, &c.

Carbonic anhydride—which, like water, is formed with the development of a large amount of heat—is very stable. Hence only very few substances are capable of depriving it of its oxygen. However, certain metals, such as magnesium, potassium, and the like, burn in it, depositing carbon and forming oxides. If a mixture of carbonic anhydride and hydrogen be passed through a heated tube, formation of water and carbonic oxide will be observed; $CO_2 + H_2 = CO + H_2O$. But only a portion of the carbonic acid gas undergoes this change, and the result will therefore be a mixture of carbonic anhydride, carbonic oxide, hydrogen, and water, which does not suffer further change under the action of heat.¹⁷ Although, like water, carbonic anhydride is ex-

in phenomena of this kind, upon the conditions of reaction and the properties of the substances formed.

¹⁷ Hydrogen and carbon are near akin as regards affinity towards oxygen, but it must be assumed that the affinity of hydrogen is slightly greater than that of carbon, because during the combustion of hydrocarbons the hydrogen usually burns first. Some idea of this similarity of affinity may be formed by the quantity of heat evolved. Gaseous hydrogen, H_2 , on combining with an atom of oxygen, $O = 16$, develops 69,000 heat-units if the water formed be condensed to a liquid state. If the water remains in the form of a gas (steam), the latent heat of evaporation must be subtracted, and then 58,000 calories will be developed. Carbon, C , as a solid, on combining with $O_2 = 32$, develops about 97,000 calories, forming gaseous CO_2 . If it were gaseous like hydrogen, and only contained C_2 in its molecule, much more heat would be developed, and judging by other substances, whose molecules on passing from the solid to the gaseous state absorb about 10,000 to 15,000 calories, it must be held that gaseous carbon on forming gaseous carbonic anhydride would develop not less than 110,000 calories—that is, approximately twice as much as is developed in the formation of water. And since there is twice as much oxygen in a molecule of carbonic anhydride as in a molecule of water, the oxygen develops approximately the same quantity of heat on combining with hydrogen as with carbon. That is to say, that here we find the same close affinity (see Chap. II., note 7), determined by the quantity of heat, as between hydrogen, zinc, and iron. For this reason here also, as in the case of hydrogen and iron, we ought to expect an equal distribution of oxygen between hydrogen and carbon, if they are both in excess compared with the amount of oxygen; but if there be an excess of carbon, it will decompose water, whilst an excess of hydrogen will decompose carbonic anhydride. P. Sabatier and Senderens (1902) showed that at 350° finely powdered nickel (reduced from the oxide) entirely converts a mixture of carbonic acid gas and hydrogen into methane and water, if the proportion of hydrogen be not less than is required by the equation: $CO_2 + 4H_2 = CH_4 + 2H_2O$. This is another instance in which hydrogen takes up the oxygen from CO_2 , but the affinity of carbon for hydrogen also probably influences the course of the reaction.

ceedingly stable, still on being heated it partially decomposes into carbonic oxide and oxygen. Deville showed that such is the case if carbonic anhydride be passed through a long tube containing pieces of porcelain and heated to 1300° . If the products of decomposition—namely, the carbonic oxide and oxygen—be suddenly cooled, they can, to some extent, be collected separately, although they partly reunite. A similar decomposition of carbonic anhydride into carbonic oxide and oxygen takes place on passing a series of electric sparks through it (for instance, in the eudiometer). Under these conditions an increase of volume occurs, because two volumes of CO_2 give two volumes of CO and one volume of O . The decomposition reaches a certain limit (less than one-third) and does not proceed further, so that the result is a mixture of carbonic anhydride, carbonic oxide, and oxygen, which is not altered in composition by the continued action of the sparks. This is readily understood, as it is a reversible reaction. If the carbonic anhydride be removed, then the residual mixture explodes when a spark is passed and forms carbonic anhydride.^{17a} If from a similar mixture the oxygen (and not the carbonic anhydride) be removed (by means of phosphorus), and a series of sparks be again passed, the decomposition is renewed. In these examples we see that a definite mixture of changeable substances is capable of arriving at a state of stable equilibrium, destroyed, however, by the removal of one of the substances composing the mixture. This is one of the instances of the influence of mass.

Although carbonic anhydride is decomposed on heating, it is nevertheless very stable at ordinary temperatures. Its decomposition, as

^{17a} The degree or relative magnitude of the dissociation of CO_2 varies with the temperature and pressure—that is, it increases with the temperature and as the pressure decreases. Deville found that in the flame of carbonic oxide burning in oxygen at a pressure of 1 atmosphere, about 40 per cent. of the CO_2 is decomposed when the temperature is about 3000° , but less than 1 per cent. at 1500° (Krafts); whilst under a pressure of 10 atmospheres about 34 per cent. is decomposed at 3300° (Mallard and Le Chatelier). It follows therefore that, under very small pressures, the dissociation of CO_2 will be considerable even at comparatively moderate temperatures, but at the temperature of ordinary furnaces (about 1000°) even under the small partial pressure of the carbonic acid, there are only small traces of decomposition which may be neglected in a practical estimation of the combustion of fuels. We may here give the molecular specific heat of CO_2 (i.e. the amount of heat required to raise the temperature of 44 units of weight of CO_2 by 1°), according to the determinations and calculations of Mallard and Le Chatelier. At constant volume the value is $C_v = 6.26 + 0.0037t$, and at constant pressure, $C_p = C_v + 2$ (see Chap. XIV., note 7). So that the specific heat of CO_2 increases rapidly with a rise of temperature: for example, at 0° (for 1 part by weight), it has at a constant pressure the value 0.188; at 1000° , 0.272; at 2000° , about 0.356. The cause of this must be looked for in dissociation. T. M. Cheltzoff, however, upon the basis of his researches upon explosives considers that it must be admitted that a maximum is reached at a certain temperature (about 2500°), beyond which the specific heat begins to fall.

effected by plants, is on this account all the more remarkable ; in this case the whole of the oxygen of the carbonic anhydride is separated in the free state. The mechanism of this change is that the heat and light absorbed by the plants are expended in the decomposition of the carbonic anhydride. This accounts for the enormous influence of temperature and light on the growth of plants. But it is at present not clearly understood how this takes place, or by what separate intermediate reactions the whole process of decomposition of carbonic anhydride in plants into oxygen and the carbohydrates (note 1) remaining in them, takes place. It is known that sulphurous anhydride (in many ways resembling carbonic anhydride) under the action of light (and also of heat) forms sulphur and sulphuric anhydride, SO_3 , and in the presence of water, sulphuric acid. But no similar decomposition has been obtained directly with carbonic anhydride, although it forms an exceedingly easily decomposable higher oxide—percarbonic acid ;¹⁸ and it is perhaps for this reason that the oxygen separates. On the other hand, it is known that plants always form and contain **organic acids**, and these must be regarded as derivatives of carbonic acid, as is shown by all their reactions, of which we shall shortly treat. For this reason it might be thought that the carbonic acid absorbed by the plants first forms (according to Baeyer) formic aldehyde, CH_2O , and from this organic acids, and that these latter in their final transformation yield all the other complex organic substances of plants. Many organic acids are found in plants in considerable quantity ; for instance, tartaric acid, $\text{C}_4\text{H}_6\text{O}_6$, found in grape-juice and in the acid juice of many plants ; malic acid, $\text{C}_4\text{H}_6\text{O}_5$, found not only in unripe apples but in still larger quantities in mountain-ash berries ; citric acid, $\text{C}_6\text{H}_8\text{O}_7$, found in the acid juice of lemons, in gooseberries, cranberries, &c. ; oxalic acid, $\text{C}_2\text{H}_2\text{O}_4$, found in wood-sorrel and

¹⁸ Percarbonic acid, H_2CO_4 ($= \text{H}_2\text{CO}_3 + \text{O}$) is supposed by A. Bach (1893) to be formed from carbonic acid in the action of light upon plants (in the same manner as, according to the above scheme, sulphuric acid is formed from sulphurous) with the formation of carbon, which remains in the form of hydrates of carbon : $3\text{H}_2\text{CO}_3 = 2\text{H}_2\text{CO}_4 + \text{CH}_2\text{O}$. This substance CH_2O expresses the composition of formic aldehyde which, according to Baeyer, by polymerisation and further changes, gives other hydrates of carbon and forms the first product formed in plants from CO_2 . And Berthelot (1872) had already, at the time of the discovery of persulphuric (Chap. XX.) and pernitric (Chap. VI., note 26) acids, pointed out the formation of the unstable percarbonic anhydride, CO_3 . Thus, notwithstanding the hypothetical nature of the above equation, it may be admitted, all the more readily because it explains the comparative abundance of peroxide of hydrogen (Schöne, Chap. IV.) in the air, and this also at the period of the most energetic growth of plants (in July), because percarbonic acid should, like all peroxides, easily give H_2O_2 . Percarbonic acid as such probably cannot exist, but it may be regarded as a compound of H_2O_2 and CO_2 ; its salts apparently do exist as unstable products of the action of H_2O_2 on carbonates, but our knowledge of them is incomplete.

many other plants. Sometimes these acids exist in a free state in the plants, and sometimes in the form of salts; for instance, tartaric acid is met with in grapes as the salt known as cream of tartar, but in the impure state called argol, or tartar, $C_4H_5KO_6$. There is a very clear connection between carbonic anhydride and the above-mentioned organic acids—namely, the latter, under one condition or another, all yield carbonic anhydride, and can all be formed by means of it from substances destitute of acid properties. The following examples afford the best demonstration of this fact; if acetic acid, $C_2H_4O_2$, the acid of vinegar, be passed in the form of vapour through a heated tube, it splits up into carbonic anhydride and marsh gas $= CO_2 + CH_4$. But conversely it can also be obtained from those components into which it decomposes. If one equivalent of hydrogen in marsh gas is replaced (by indirect means) by sodium, the compound CH_3Na is obtained, and this directly absorbs carbonic anhydride, forming a salt of acetic acid, $CH_3Na + CO_2 = C_2H_3NaO_2$. The hydrogen of marsh gas does not, like that in acids, show the property of being directly replaced by metals; i.e., CH_4 does not show any acid character whatever, but on combining with the elements of carbonic anhydride it acquires the properties of an acid. The investigation of all other organic acids shows similarly that their acid character depends on their containing the elements of carbonic anhydride. For this reason there is no organic acid containing less oxygen in its molecule than is present in carbonic anhydride; every organic acid, like carbonic acid, contains in its molecule at least two atoms of oxygen. If the addition of CO_2 raises the basicity, the removal of CO_2 lowers it. Thus from the dibasic oxalic acid, $C_2H_2O_4$, and phthalic acid, $C_8H_6O_4$, by eliminating CO_2 (easily effected experimentally) we obtain monobasic formic acid, CH_2O_2 , and benzoic acid, $C_7H_6O_2$ respectively. This shows that a group, HCO_2 , or **carboxyl**, must be recognised in organic acids. If we take a hydrocarbon compound A, not having the properties of an acid, but containing hydrogen united to carbon, as in the hydrocarbons, then ACO_2 will be a monobasic organic acid, A_2CO_2 a dibasic acid, A_3CO_2 a tribasic acid, and so on. That is, each molecule of CO_2 converts one hydrogen into the form in which it is capable of being replaced by metals, as in acids. The nature of carboxyl is directly explained by the law of substitution. Judging from what has been stated in Chapters VI. and VIII. concerning this law, it is evident that CO_2 is CH_4 with the H_4 exchanged for O_2 , and that the hydrate of carbonic anhydride, H_2CO_3 , is $CO(OH)_2$, that is, methane, in which two parts of hydrogen are replaced by two parts of the water radicle (OH, hydroxyl) and the other two by oxygen. Therefore the group $CO(OH)$, or carboxyl, HCO_2 ,

is a part of carbonic acid, and is equivalent to (OH), and therefore also to H. That is, it is a univalent residue of carbonic acid capable of replacing one atom of hydrogen. Carbonic acid itself is a dibasic acid, both hydrogen atoms in it being replaceable by metals, so that carboxyl, which contains one of the hydrogen atoms of carbonic acid, represents a group in which the hydrogen is exchangeable for metals. And therefore if 1, 2 . . . n atoms of non-metallic hydrogen are exchanged 1, 2 . . . n times for carboxyl, we ought to obtain 1-, 2- . . . n -basic acids. *Organic acids are the products of carboxyl substitution in hydrocarbons.*^{18a} If in the saturated hydrocarbons, C_nH_{2n+2} , one part of hydrogen be replaced by carboxyl, the monobasic saturated (or fatty) acids, $C_nH_{2n+1}(CO_2H)$, will be obtained, as, for instance, formic acid, HCO_2H , acetic acid, CH_3CO_2H , . . . stearic acid, $C_{17}H_{35}CO_2H$, &c. The double substitution will give dibasic acids, $C_nH_{2n}(CO_2H)(CO_2H)$; for instance, in oxalic acid $n = 0$, in malonic acid $n = 1$, and in succinic acid $n = 2$, &c. To benzene, C_6H_6 , correspond benzoic acid, $C_6H_5(CO_2H)$, phthalic acid (and its isomerides), $C_6H_4(CO_2H)_2$, and so on, up to mellitic acid, $C_6(CO_2H)_6$, in all of which the basicity is equal to the number of carboxyl groups. As many isomerides exist in hydrocarbons, it is readily understood not only that such can exist also in organic acids, but that their number and structure may be foreseen. This complex and most interesting branch is treated of separately in organic chemistry.

Carbonic Oxide.—This gas is formed whenever the combustion of

^{18a} If CO_2 is the anhydride of a dibasic acid, and carboxyl corresponds with it, replacing the hydrogen of hydrocarbons, and giving them the character of comparatively feeble acids, then SO_3 is the anhydride of an energetic dibasic acid, and *sulphoxyl*, $SO_2(OH)$, corresponds with it, being capable of replacing the hydrogen of hydrocarbons, and forming comparatively energetic *sulphur oxyacids* (*sulphonic acids*); for instance, $C_6H_5(COOH)$, benzoic acid, and $C_6H_5(SO_2OH)$, benzenesulphonic acid, are derived from C_6H_6 . Just as the exchange of H for methyl, CH_3 , is equivalent to the addition of CH_2 , so the exchange of carboxyl, $COOH$, is equivalent to the addition of CO_2 ; also the replacement of H by sulphoxyl is equivalent to the addition of SO_3 . The latter proceeds directly, for instance: $C_6H_6 + SO_3 = C_6H_5(SO_2OH)$.

As, according to the determinations of Thomsen, the heat of combustion of the *vapours* of acids RCO_2 is known where R is a hydrocarbon, and also the heats of combustion of the hydrocarbons R themselves, it can be shown that the formation of acids, RCO_2 , from $R + CO_2$ is always accompanied by a *small* absorption or development of heat. We give the heats of combustion in thousands of calories, referred to the molecular weights of the substances:—

	R		
	H ₂	CH ₄	C ₂ H ₆
Hydrocarbon	68·4	212	370
Acid RCO_2	69·4	225	387

Benzene, C_6H_6 , gives 777 and benzoic acid, $C_7H_6O_2$, 766 thousands of calories. The data for the latter are taken from Stohmann, and refer to the solid condition.

organic substances takes place in the presence of a large excess of incandescent charcoal; the air first burns the carbon into carbonic anhydride, but this in penetrating through the red-hot charcoal is transformed into carbonic oxide, $\text{CO}_2 + \text{C} = 2\text{CO}$. By this reaction carbonic oxide is prepared by passing carbonic anhydride through charcoal at a red heat. (The reaction does not proceed to the end.) It may be separated from the excess of carbonic anhydride by passing it through a solution of alkali, which does not absorb carbonic oxide. This reduction of carbonic anhydride explains why carbonic oxide is formed in ordinary clear fires, where the incoming air passes over a large surface of heated coal. A blue flame is then observed burning above the coal; this is the burning carbonic oxide. When charcoal is burnt in stacks, when a thick layer of coal is burning in a brazier, and under many similar circumstances, carbonic oxide is also formed. In metallurgical processes, for instance, when iron is smelted from the ore, very often the same process of conversion of carbonic anhydride into carbonic oxide occurs, especially if the combustion of the coal be effected in tall, so-called blast, furnaces and ovens, where the air enters at the lower part and is compelled to pass through a thick layer of incandescent coal. In this way, also, combustion with flame may be obtained from those kinds of fuel which under ordinary conditions burn without flame; for instance, anthracite, coke, charcoal. Heating by means of a **gas-producer**—that is, an apparatus producing combustible carbonic oxide from fuel—is carried on in the same manner.¹⁹ In transforming one part of charcoal into carbonic oxide 2,420 heat units are given out, and on burning to carbonic anhydride 8,080 heat units. It is evident that on transforming the charcoal first into carbonic oxide we obtain a gas which in burning is capable of giving out 5,660 heat units for one part of charcoal. This preparatory transformation of fuel into carbonic oxide, or producer gas containing a mixture of carbonic oxide (about $\frac{1}{3}$ by volume) and nitrogen ($\frac{2}{3}$ volume), in many cases presents most important advantages,

¹⁹ In gas-producers all carbonaceous fuels are transformed into inflammable gas. In those which (on account of their slight density and large amount of water, or combustible admixtures which absorb heat) are not as capable of giving a high temperature in ordinary furnaces—for instance, fir cones, peat, the lower kinds of coal, &c.—the same gas is obtained as with the best kinds of coal, because the water condenses on cooling, and the ashes and earthy matter remain in the gas producer. The construction of a gas-producer is seen from the accompanying drawing. The fuel lies on the fire-bars O, through which and the ash-hole the air enters (drawn by the draught of the chimney of the stove where the gas burns, or else forced by a blowing apparatus), the quantity of air being regulated exactly by means of valves. The gases formed are then led by the pipe V, provided with a valve, into the gas main U. The addition of fuel ought to proceed in such a way as to prevent the generated gas escaping; hence the space A is kept filled with the combustible material and covered with a lid.

as it is easy to completely burn gaseous fuel without an excess of air, which would lower the temperature.²⁰ In stoves where solid fuel is burnt it is impossible to effect the complete combustion of the various kinds of fuel without admitting an excess of air. Gaseous fuel, such as carbonic oxide, is easily completely mixed with air and burnt without excess of it. If, in addition to this, the air and gas required for the combustion be previously heated by means of the heat which would otherwise be uselessly carried off in the products of combustion (smoke)²¹, it is easy to reach a high temperature, so high (about 1800°) that platinum may be melted. Such an arrangement is known as a *regenerator furnace*.²² By means of this process not only may the high temperatures indispensable in many industries be obtained (for instance, glass-working, steel-melting, &c.), but a great advantage is also ²³ gained as regards the quantity of fuel, because the transmission of heat to the

²⁰ An excess of air lowers the temperature of combustion, because it becomes heated itself, as explained in Chap. III. In ordinary furnaces the excess of air is three or four times greater than the quantity required for perfect combustion. In the best furnaces (with fire-bars, regulated air supply, and corresponding chimney draught) it is necessary to introduce $1\frac{1}{2}$ time as much air as is necessary, otherwise the smoke contains much carbonic oxide.

²¹ If in manufactories it is necessary, for instance, to maintain the temperature in a furnace at 1000°, the flame passes out at this or a higher temperature, and therefore much heat is lost in the smoke. For the draught of the chimney a temperature of 100° to 150° is sufficient, and therefore the remaining heat ought to be utilised. For this purpose the flues are carried under boilers or other heating apparatus. The preparatory heating of the air is the best means of utilisation when a high temperature is desired (see note 22).

²² Regenerator furnaces were introduced into many industries by the Brothers Siemens about the year 1860, and mark a most important progress in the use of fuel, especially in obtaining high temperatures. The principle is as follows: The products of combustion from the furnace are led into a chamber, I, and heat up the bricks in it, and then pass into the outlet flue; when the bricks are at a red heat the products of combustion are passed (by altering the valves) into another adjoining chamber, II, and air requisite for the combustion of the generator gases is passed through I. In passing round about the incandescent bricks the air is heated, and the bricks cooled—that is, the heat of the smoke is returned into the furnace. The air is then passed through II, and the smoke through I. The regenerator burners for illuminating gas are based on this same principle; the products of combustion heat the incoming air and gas, the temperature is higher, the light brighter, and an economy of gas is effected.

²³ At first sight it appears absurd, useless, and paradoxical to lose nearly one-third of the heat which fuel can develop, by turning it into gas. In reality, however, the advantage is enormous, especially for producing high temperatures, as is already seen from the fact that fuels rich in oxygen (for instance, wood) when damp are unable, with any kind of hearth whatsoever, to give the temperature required for glass-melting or steel-casting, whilst in the gas-producer they furnish exactly the same gas as the driest and most carbonaceous fuel. In order to understand the principle which is here involved, it is sufficient to remember that a large amount of heat at a low temperature is in many cases of no use whatever. We are unable here to enter into all the details of the complicated matter of the application of fuel, and further particulars must be sought for in special technical treatises.

object to be heated, other conditions being equal, is determined by the difference of temperatures.

The transformation of carbonic anhydride, by means of charcoal, into carbonic oxide ($C + CO_2 = CO + CO$) is considered a reversible reaction, because at a high temperature the carbonic oxide splits up into carbon and carbonic anhydride, as Sainte-Claire Deville showed by using the method of the 'cold and hot tube.' Inside a tube heated in a furnace is fitted another thin metallic (silver copper) tube, through which a constant stream of cold water flows. The carbonic oxide coming into contact with the heated walls of the exterior tube forms charcoal, the minute particles of which settle in the form of lampblack on the lower side of the cold tube, and, since they are cooled, do not act further on the oxygen or carbonic anhydride formed.²⁴

²⁴ The first product of combustion of charcoal is always carbonic anhydride, and not carbonic oxide. This is seen from the fact that with a shallow layer of charcoal (less than a decimetre if the charcoal be closely packed) carbonic oxide is not formed at all. It is not even produced with a deep layer of charcoal if the temperature is not above 500° and the current of air or oxygen is very slow. With a rapid current of air the charcoal becomes red-hot, and the temperature rises, and then carbonic oxide appears (Lang, 1888). Ernst (1891) found that below 995° carbonic oxide is always accompanied by CO_2 , and that the formation of CO_2 begins about 400° . Naumann and Pistor determined that the reaction of carbonic anhydride with carbon commences at about 550° , and that between water and carbon at about 500° . At the

latter temperature carbonic anhydride is formed, and only with a rise of temperature is carbonic oxide formed (Lang) from the action of the carbonic anhydride on the carbon, and also from the reaction $CO_2 + H_2 = CO + H_2O$. Rathke (1881) showed that at no temperature whatever is the reaction as expressed by the equation, $CO_2 + C = 2CO$, complete; a part of the carbonic anhydride remains, and Lang determined that at about 1000° not less than 3 per cent. of the carbonic anhydride remains untransformed into carbonic oxide, even after the action has been continued for several hours. The endothermic reactions, $C + 2H_2O = CO_2 + 2H_2$, and $CO + H_2O = CO_2 + H_2$, are just as incomplete. This is made clear if we note, on the one hand, that the above-mentioned reactions are all *reversible*, and therefore bounded by a limit; and, on the other, that at about 500° oxygen begins to combine with hydrogen and carbon and also that the lower limits of dissociation of water, carbonic anhydride, and carbonic oxide lie near one another between 500° and $1,200^\circ$. For water and carbonic oxide the lower limit of the commencement of dissociation is unknown, but judging from the published data

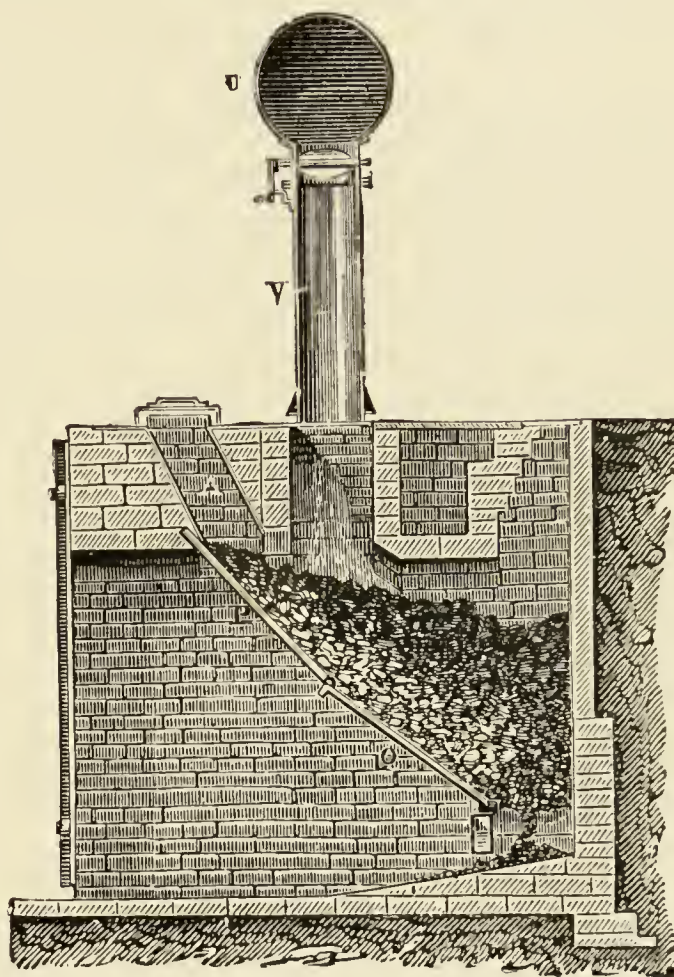


FIG. 72.—Gas-producer for the formation of carbon monoxide for heating purposes.

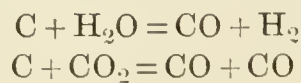
A series of electric sparks also decomposes carbonic oxide into carbonic anhydride and carbon, and, if the carbonic anhydride be removed by alkali, complete decomposition may be obtained (Dewille).^{24a} Aqueous vapour, which is so similar to carbonic anhydride in many respects, acts, at a high temperature, on charcoal in an exactly similar way, $C + H_2O = H_2 + CO$. From 2 volumes of carbonic anhydride with charcoal 4 volumes of carbonic oxide (2 molecules) are obtained, and so also from 2 volumes of water vapour with charcoal 4 volumes of a gas consisting of hydrogen and carbonic oxide ($H_2 + CO$) are formed. This mixture of combustible gases is called **water gas**.²⁵ But aqueous vapour (and only when strongly superheated, otherwise it cools the charcoal) only acts on charcoal to form a large amount of carbonic oxide at a very

(according to Le Chatelier, 1888) that of carbonic anhydride may be taken as about 1050° . Even at about 2000° half the carbonic anhydride dissociates if the pressure be small,—about 0.001 atmosphere. At the atmospheric pressure, not more than 0.05 per cent. of the carbonic anhydride decomposes. The reason of the influence of pressure is here evidently that the splitting up of carbonic anhydride into carbonic oxide and oxygen is accompanied by the increase in volume (as in the case of the dissociation of nitric peroxide. See Chap. VI., note 46). As in stoves and lamps, and also with explosive substances, the temperature is not higher than 2000° to 2500° , it is evident that although the partial pressure of carbonic anhydride is small, still its dissociation cannot here be considerable, and probably does not exceed 5 per cent.

^{24a} Besides which, L. Mond (1890) showed that the powder of freshly reduced metallic nickel (obtained by heating the oxide to redness in a stream of hydrogen) is able, when heated even to 350° , to *completely* decompose carbonic oxide into CO_2 and carbon, which remains with the nickel and is easily removed from it by heating in a stream of air. Here $2CO = CO_2 + C$. It should be remarked that heat is evolved in this reaction (note 25), and therefore that the influence of 'contact' may here play a part. Indeed, this reaction must be classed among the most remarkable instances of the influence of contact, especially as metals analogous to Ni (Fe and Co) do not effect this reaction (see Chap. II., note 17).

²⁵ A molecular weight of this gas, or 2 volumes of CO (28 grams), on combustion (forming CO_2) gives out 68,000 heat units (Thomsen 67,960 calories). A molecular weight of hydrogen, H_2 (or 2 volumes), develops on burning into *liquid* water 69,999 heat units (according to Thomsen 68,300), but if it forms aqueous *vapour*, 58,000 heat units. Charcoal, resolving itself by combustion into the molecular quantity of CO_2 (2 volumes), develops 97,000 heat units. From the data furnished by the exothermic reactions it follows: (1) that the oxidation of charcoal into carbonic oxide develops 29,000 heat units; (2) that the reaction $C + CO_2 = 2CO$ *absorbs* 39,000 heat units; (3) $C + H_2O = H_2 + CO$ *absorbs* (if the water be in a state of vapour) 29,000 calories, but if the water be liquid, 40,000 calories (almost as much as $C + CO_2$); (4) $C + H_2O = CO_2 + 2H_2$ *absorbs* (if the water be in a state of vapour) 19,000 heat units; (5) the reaction $CO + H_2O = CO_2 + H_2$ *develops* 10,000 heat units if the water be in the state of vapour; and (6) the decomposition expressed by the equation $2CO = C + CO_2$ (note 24a) is accompanied by the *evolution* of 39,000 units of heat.

Hence it follows that 2 volumes of CO or H_2 burning into CO_2 or H_2O develop almost the same amount of heat, just as also the heat effects corresponding with the equations:



re nearly equal.

high temperature (at which carbonic anhydride dissociates); it begins to react at about 500° , forming carbonic anhydride according to the equation: $C + 2H_2O = CO_2 + 2H_2$. Besides this, carbonic oxide on splitting up forms carbonic anhydride, and therefore water gas always contains a mixture ²⁶ in which hydrogen predominates, the volume of carbonic oxide being comparatively less, whilst the amount of carbonic anhydride increases as the temperature of the reaction decreases (generally it is more than 3 per cent.).

Metals like iron and zinc, which at a red heat are capable of decomposing water with the formation of hydrogen, also decompose carbonic anhydride with the formation of carbonic oxide; thus both the ordinary products of complete combustion, water and carbonic anhydride, are very similar in their reactions. The metallic oxides of the above-mentioned metals, when reduced by charcoal, also give carbonic oxide.

²⁶ **Water gas**, obtained from steam and charcoal at a white heat, contains about 50 per cent. (by volume) of hydrogen, about 40 of carbonic oxide, and about 5 of carbonic anhydride, the remainder being nitrogen from the charcoal and air. Compared with producer gas, which contains much nitrogen, this is a gas much richer in combustible matter, and therefore capable of giving high temperatures, and is for this reason of the greatest utility. If carbonic anhydride could be as readily obtained in as pure a state as water, then CO might be prepared directly from $CO_2 + C$, and in that case the utilisation of the heat of the carbon would be the same as in water gas, because CO evolves as much heat as H_2 , and even more if the temperature of the products formed is over 100° , and the water remains in the form of vapour (note 25). But producer gas contains a large proportion of nitrogen, so that its effective temperature is below that given by water gas; therefore in places where a particularly high temperature is required (for instance for lighting by means of incandescent lime or magnesia, or for melting steel, &c.), and where the gas can be easily distributed through pipes, water gas is at present held in high estimation, but when (in ordinary furnaces, re-heating, glass-melting, and other furnaces) a very high temperature is not required, and there is no need to convey the gas in pipes, producer gas is generally preferred on account of the simplicity of its preparation, especially as for water gas such a high temperature is required that the plant soon becomes damaged.

There are numerous systems for making water gas, but the American patent of T. Lowe is generally used. The gas is prepared in a cylindrical generator, into which hot air is introduced, in order to raise the coke in it to a white heat. The products of combustion containing carbonic oxide are utilised for superheating steam, which is then passed over the white hot coke. Water gas, or a mixture of hydrogen and carbonic oxide, is thus obtained.

Water gas is sometimes called the '*fuel of the future*,' because it is applicable to all purposes, develops a high temperature, and is therefore available, not only for domestic and industrial uses, but also for gas-motors and for lighting. For the latter purpose platinum, lime, magnesia, zirconia, and similar substances (as in the Drummond light (Chap. III.) are rendered incandescent in the flame, or else the gas is **carburetted**—that is, mixed with the vapours of volatile hydrocarbons (generally benzene or naphtha, naphthalene, or simply naphtha gas), which communicate to the pale flame of carbonic oxide and hydrogen a great brilliancy, owing to the high temperature developed by the combustion of the non-luminous gases. In some cases *Dowson gas* is prepared in producers. This is a mixture of water and producer gases obtained by passing steam into an ordinary producer (note 19), when the temperature of the carbon has become sufficiently high for the reaction, $C + H_2O = CO + H_2$.

Priestley obtained it by heating charcoal with zinc oxide. As free carbonic anhydride may be transformed into carbonic oxide, so, in precisely the same way, may that carbonic acid which is in a state of combination; hence, if magnesium or barium carbonate (MgCO_3 or BaCO_3) be heated to redness with charcoal, or iron, or zinc, carbonic oxide will be produced—it is obtained, for instance, by heating an intimate mixture of 9 parts of chalk and 1 part of charcoal in a clay retort, or by passing carbonic acid gas over hot zinc dust: $\text{Zn} + \text{CO}_2 = \text{ZnO} + \text{CO}$.

Many organic substances²⁷ on being heated, or under the action of various reagents, yield carbonic oxide; amongst these are many organic or carboxylic acids, the simplest being formic and oxalic acids. Formic acid, CH_2O_2 , on being heated to 200° , readily decomposes into carbonic oxide and water, $\text{CH}_2\text{O}_2 = \text{CO} + \text{H}_2\text{O}$.^{27a} Usually, however, carbonic oxide is prepared in laboratories, not from formic but from oxalic acid, $\text{C}_2\text{H}_2\text{O}_4$, which is easily obtained by the action of nitric acid on starch, sugar, &c.; it is also found in nature, and is used in the arts. Oxalic acid is easily decomposed by heat; its crystals first lose water, then partly volatilise, but the greater part is decomposed. In this decomposition the acid splits up into water, carbonic oxide, and carbonic anhydride,²⁸ $\text{C}_2\text{H}_2\text{O}_4 = \text{H}_2\text{O} + \text{CO}_2 + \text{CO}$. This decomposition is generally effected practically by mixing oxalic acid with strong sulphuric acid, because the latter assists the decomposition by taking up the water. On heating a mixture of oxalic and sulphuric acids a mixture of carbonic oxide and carbonic anhydride is evolved. This mixture is passed through a solution of an alkali in order to absorb the carbonic anhydride, the carbonic oxide passing on.

In its physical **properties** carbonic oxide resembles nitrogen; this is explained by the equality of their molecular weights. The absence

²⁷ The so-called yellow prussiate of potash, $\text{K}_4\text{FeC}_6\text{N}_6$, on being heated with ten parts of strong sulphuric acid yields a considerable quantity of very pure carbonic oxide quite free from carbonic anhydride. Greshoff (1888) showed that iodoform, CHI_3 , and a solution of nitrate of silver directly give CO *in toto* according to the equation, $\text{CHI}_3 + 3\text{AgNO}_3 + \text{H}_2\text{O} = 3\text{AgI} + 3\text{HNO}_3 + \text{CO}$, and Thiele and Dent obtained CO by the action of a strong solution of caustic potash on chloroform, $\text{CHCl}_3 + 3\text{KHO} = 3\text{KCl} + 2\text{H}_2\text{O} + \text{CO}$.

^{27a} To perform this reaction, the formic acid is mixed with glycerine, because when heated alone it volatilises much below its temperature of decomposition. When heated with sulphuric acid the salts of formic acid yield carbonic oxide.

²⁸ The decomposition of formic and oxalic acids, with the formation of carbonic oxide, considering these acids as carboxyl derivatives, may be explained as follows:—The first is $\text{H}(\text{CO}_2\text{H})$ and the second $(\text{CO}_2\text{H})_2$, or H_2 , in which one or both halves of the hydrogen are exchanged for carboxyl; therefore they are equal to $\text{H}_2 + \text{CO}_2$ and $\text{H}_2 + 2\text{CO}_2$; but H_2 reacts with CO_2 , as has been stated above, forming CO and H_2O . From this it is also evident that oxalic acid on losing CO_2 forms formic acid, and also that the latter may proceed from $\text{CO} + \text{H}_2\text{O}$, as we shall see further on. Citric acid, $\text{C}_6\text{H}_8\text{O}_7$, also gives CO when heated with strong sulphuric acid.

of colour and smell, the low temperature of the absolute boiling-point, -140° (nitrogen, -146°), the property of solidifying at -200° (nitrogen, -202°), the boiling-point of -190° (nitrogen, -203°), and the slight solubility (Chapter I., note 30) of carbonic oxide are almost the same as with nitrogen. The chemical properties of the two gases are, however, very different, and in these carbonic oxide resembles hydrogen. Carbonic oxide burns with a blue flame like hydrogen, and it explodes with oxygen, in the eudiometer.²⁹ When breathed it acts as a strong poison, being absorbed by the blood; ³⁰ this explains the action of charcoal fumes, the products of the incomplete combustion of charcoal and other carbonaceous fuels.

Owing to its power of combining with oxygen, carbonic oxide acts as a powerful **reducing agent**, taking up the oxygen from many compounds at a red heat, and being itself transformed into carbonic anhydride. The reducing action of carbonic oxide, however, is (like that of hydrogen, Chapter II.) naturally confined to those oxides which readily part with their oxygen—as, for instance, copper oxide—whilst the oxides of magnesium or potassium are not reduced. Metallic iron itself is capable of reducing carbonic anhydride to carbonic oxide, just as it liberates the hydrogen from water. Copper, however, which does not decompose water, does not decompose carbonic oxide. If a platinum wire heated to 300° , or spongy platinum at the ordinary temperature,

²⁹ It is remarkable that, according to the investigations of Dixon, perfectly dry carbonic oxide does not explode with oxygen when a spark of low intensity is used, but an explosion takes place if there is the slightest admixture of moisture. L. Meyer, however, showed that sparks of an electric discharge of considerable intensity produce an explosion. I think that this may be explained by the fact that water with carbonic oxide gives carbonic anhydride and hydrogen, but hydrogen with oxygen gives hydrogen peroxide (Chap. VII.), which with carbonic oxide forms carbonic anhydride and water. The water, therefore, is renewed, and again serves the same purpose. But it may be that here it is necessary to acknowledge a simple contact influence. After Dixon had shown the influence of traces of moisture upon the reaction $\text{CO} + \text{O}$, many researches of a similar nature were made. The fullest investigation into the influence of moisture upon the course of many chemical reactions was made by Baker in 1894. He showed that with perfect dryness many chemical transformations (for example, the formation of ozone from oxygen, the decomposition of HgO , KClO_3 under the action of heat, &c.) proceed in exactly the same manner as in the presence of moisture; but that in many cases traces of moisture have an evident influence. We may mention the following instances: (1) Dry SO_3 does not act upon dry CaO or CuO ; (2) perfectly dry sal-ammoniac does not give NH_3 with dry CaO , but simply volatilises; (3) dry NO and O do not react; (4) perfectly dry NH_3 and HCl do not combine; (5) perfectly dry sal-ammoniac does not dissociate at 350° (Chap. VII., note 15a); and (6) perfectly dry chlorine does not act upon metals, &c.

³⁰ Carbonic oxide is very rapid in its action, because it is absorbed by the blood in the same way as oxygen. In addition to this, the absorption spectrum of the blood changes, so that by the help of blood it is easy to detect the slightest traces of carbonic oxide in the air. M. A. Kapoustin found that linseed oil, and therefore oil paints, are capable of giving off carbonic oxide while drying (absorbing oxygen).

be plunged into a mixture of carbonic oxide and oxygen, the mixture explodes like a mixture of $H_2 + O$. These reactions are very similar to those peculiar to hydrogen.^{30a} The following important distinction, however, exists between them—namely: the molecule of hydrogen is composed of H_2 , a group of elements divisible into two like parts, whilst, as the molecule of carbonic oxide, CO , contains unlike atoms of carbon and oxygen, in none of its reactions of combination can it give two molecules of matter containing its elements. This is particularly noticeable in the action of chlorine on hydrogen and on carbonic oxide respectively; with the former chlorine forms hydrogen chloride, and with the latter it produces the so-called carbonyl chloride, $COCl_2$; that is to say, the molecule of hydrogen, H_2 , under the action of chlorine divides, forming two molecules of hydrochloric acid, whilst the molecule of carbonic oxide enters in its entirety into the molecule of carbonyl chloride. This characterises the reactions of so-called **diatomic** or **bivalent** radicles or **residues**. H is a monatomic residue or radicle, like K , Cl , and others, whilst carbonic oxide, CO , is an indivisible (without decomposition) bivalent radicle, equivalent to H_2 and not to H , and therefore combining with X_2 and interchangeable with H_2 . This distinction is evident from the annexed comparison:—

HH , hydrogen.	CO , carbonic oxide.
HCl , hydrochloric acid.	$COCl_2$, carbonyl chloride.
HKO , potash.	$CO(KO)_2$, potassium carbonate.
HNH_2 , ammonia.	$CO(NH_2)_2$, urea.
HCH_3 , methane.	$CO(CH_3)_2$, acetone.
HHO , water.	$CO(HO)_2$, carbonic acid.
H_2O , water.	COO , carbonic acid gas.

Such monatomic (univalent) residues, X , as H , Cl , Na , NO_2 , NH_4 , CH_3 , CO_2H (carboxyl), OH , and others, in accordance with the law of substitution, combine together, forming compounds, XX' ; and with oxygen, or in general with diatomic (bivalent) residues, Y —for instance, O , CO , CH_2 , S , Ca , &c. forming compounds $XX'Y$; but diatomic residues, Y , sometimes capable of existing separately may combine together, forming YY' and with X_2 or XX' , as we see from the transition of CO into CO_2 and $COCl_2$. This combining power of carbonic oxide appears in many of its reactions. Thus it is very easily absorbed by cuprous chloride, $CuCl$, dissolved in fuming hydrochloric acid, forming a crystalline compound, $COCu_2Cl_2 \cdot 2H_2O$, decomposable by

^{30a} Formaldehyde (the aldehyde of formic acid), CH_2O , which is obtained by oxidising methyl alcohol, and readily yields solid polymerides, acts as a powerful reducing agent owing to the fact that it contains the elements $CO + H_2$, just as phosgene contains $CO + Cl_2$.

water; it combines directly with potassium (at 90°), forming $(\text{KCO})_n$,³¹ with platinum dichloride, PtCl_2 , with chlorine, Cl_2 , &c.

But the most remarkable compounds are: (1) the compound of CO with metallic nickel, a colourless volatile liquid, $\text{Ni}(\text{CO})_4$, obtained by L. Mond (and described in Chap. XXII.) and (2) the compounds of carbonic oxide with the alkalis, for instance, with potassium or barium hydroxide, &c.—although it is not directly absorbed by them, as it has no acid properties. Berthelot (1861) showed that potash in the presence of water is capable of absorbing carbonic oxide, but the absorption takes place very gradually, and it is only after being heated for many hours that the whole of the carbonic oxide is absorbed by the potash. The salt CHKO_2 is obtained by this absorption; it corresponds with an acid found in nature—namely, the simplest organic (carboxylic) acid, **formic acid**, CH_2O_2 . It can be extracted from the potassium salt by means of distillation with dilute sulphuric acid, just as nitric acid is prepared from sodium nitrate. This same acid is found in ants and in nettles (when the stings of the nettles puncture the skin they break, and the corrosive formic acid enters into the body); it is also obtained during the action of oxidising agents on many organic substances; it is formed from oxalic acid, and under many conditions splits up into carbonic oxide and water. In the formation of formic acid from carbonic oxide we observe an example of the synthesis of organic compounds, such as are now very numerous, and are treated of in detail in works on organic chemistry. Moissan (1901) accomplished this synthesis by means of CO_2 , as he showed that sodium hydride, NaH (Chap. XII.), directly forms sodium formate, CNaHO_2 with CO_2 .

Formic acid, $\text{H}(\text{CHO}_2)$, carbonic acid, $\text{HO}(\text{CHO}_2)$, and oxalic acid, $(\text{CHO}_2)_2$, are the simplest organic or carboxylic acids, $\text{R}(\text{CHO}_2)$ corresponding with HH and HOH . Commencing with carbonic oxide, CO , the formation of carboxylic acids is clearly seen from the fact that CO is capable of combining with X_2 , that is, of forming COX_2 . If, for instance, one X is an aqueous residue, OH (hydroxyl), and the other X hydrogen, then the simplest organic acid—formic acid, $\text{H}(\text{COOH})$ —is obtained. As all hydrocarbons (Chap. VIII.) correspond with the simplest, CH_4 , so all organic acids may be considered to proceed from formic acid.

In a similar way it is easy to explain the relation to other

³¹ The black mass formed by the combination of carbonic oxide with potassium explodes with great ease, and oxidises in the air. Although Brodie, Lerch, and Joannis (who obtained it in 1893 in a colourless form by means of NH_3K , described in Chap. VI., note 14) have greatly extended our knowledge of this compound, much still remains unexplained. It probably exists in various polymeric and isomeric forms, having the composition $(\text{KCO})_n$.

compounds of carbon of those compounds which contain nitrogen. By way of an example, we will take one of the carboxyl acids, $R(\text{CO}_2\text{H})$, where R is a hydrocarbon radicle (residue). Such an acid, like all others, will give by combination with NH_3 an ammoniacal salt, $R(\text{CO}_2\text{NH}_4)$. This salt contains the elements for the formation of two molecules of water, and under suitable conditions by the action of bodies capable of taking it up, water may in fact be separated from $R(\text{CO}_2\text{NH}_4)$, forming by the loss of one molecule of water, **amides**, $R\text{CONH}_2$,³² and by the loss of two molecules of water, **nitriles**, RCN , otherwise known as **cyanogen compounds** or **cyanides**.³³ If all the carboxyl acids are united not only by many common reactions but also by mutual conversion into each other (an instance of which we saw above in the conversion of oxalic acid into formic and carbonic acids), one would expect the same for all the cyanogen compounds also. The common character of their reactions and the reciprocity of their transformation were long ago observed by Gay-Lussac, who recognised a common group or radicle (residue) cyanogen, CN , in all of them. The simplest compounds are hydrocyanic or prussic acid, HCN , cyanic acid, OHCN , and free cyanogen, $(\text{CN})_2$, which correspond to the three simplest carboxylic acids: formic, HCO_2H , carbonic, $\text{OHC}_2\text{O}_2\text{H}$, and oxalic, $(\text{CO}_2\text{H})_2$. Cyanogen, like carboxyl, is evidently a monatomic residue and of an acid nature, like chlorine.

The reactions and properties of the amides and nitriles of the organic acids are described in detail in books on organic chemistry; we will here only touch upon the simplest of them, and to clearly explain the derivative compounds will first consider the ammoniacal salts and amides of carbonic acid.

As carbonic acid is dibasic, its ammonium salts ought to have the following composition: **acid carbonate of ammonium**, $\text{H}(\text{NH}_4)\text{CO}_3$, and

³² Thus, for instance, *oxamide*, or the amide of oxalic acid, $(\text{CNH}_2\text{O})_2$, is obtained in the form of an insoluble precipitate on adding a solution of ammonia to an alcoholic solution of ethyl oxalate $(\text{CO}_2\text{C}_2\text{H}_5)_2$, which is formed by the action of oxalic acid on alcohol: $(\text{CHO}_2)_2 + 2(\text{C}_2\text{H}_5)\text{OH} = 2\text{HOH} + (\text{CO}_2\text{C}_2\text{H}_5)_2$. As the nearest derivatives of ammonia, the amides treated with alkalis yield ammonia and form the salt of the acid. The nitriles do not, however, give similar reactions so readily. The majority of amides corresponding to acids have a composition RNH_2 , and therefore recombine with water with great ease even when simply boiled with it, and with still greater facility in presence of acids or alkalis. Thus in the majority of cases amides easily pass into ammoniacal salts, but they differ essentially from them. No ammoniacal salt sublimes or volatilises unchanged, and generally when heated it gives off water and yields an amide, whilst many amides volatilise without alteration, and are frequently volatile crystalline substances which may be easily sublimed. Such, for instance, are the amides of benzoic, formic, and many other organic acids.

³³ The connection of the cyanogen compounds with the rest of the hydrocarbons by means of carboxyl was enunciated by me, about the year 1860, at the first Annual Meeting of the Russian Naturalists.

normal carbonate, $(\text{NH}_4)_2\text{CO}_3$; they represent compounds of one or two molecules of ammonia with carbonic acid. The acid salt appears in the form of a non-odoriferous and (when tested with litmus) neutral substance, soluble at the ordinary temperature in six parts of water and insoluble in alcohol. If an aqueous solution of ammonia be saturated with an excess of carbonic anhydride, and then evaporated over sulphuric acid in the bell-jar of an air-pump, crystals of this salt are separated. Solutions of all other ammonium carbonates, when evaporated under the air-pump, yield crystals of this salt. A solution of this salt, even at the ordinary temperature, gives off carbonic anhydride, as do all the acid salts of carbonic acid (for instance, NaHCO_3), and at 38° the separation of carbonic anhydride takes place with great rapidity. *On losing carbonic anhydride* and water, the acid salt is converted into the normal salt: $2(\text{NH}_4)\text{HCO}_3 = \text{H}_2\text{O} + \text{CO}_2 + (\text{NH}_4)_2\text{CO}_3$; the latter, however, decomposes in solution, with *the evolution of ammonia* and formation of the acid salt, and can therefore only be obtained in crystals, $(\text{NH}_4)_2\text{CO}_3 \cdot \text{H}_2\text{O}$, at low temperatures, and from solutions containing an *excess of ammonia*, which is one of the products of dissociation of this salt: $(\text{NH}_4)_2\text{CO}_3 = \text{NH}_3 + (\text{NH}_4)\text{HCO}_3$. But the normal salt,³⁴ according to the general type, is capable of decomposing *with separation of water*, and forming **ammonium carbamate**, $\text{NH}_4\text{O}(\text{CONH}_2) = (\text{NH}_4)_2\text{CO}_3 - \text{H}_2\text{O}$; this still further complicates the chemical transformations of the carbonates of ammonium. It is in fact evident that, by changing the ratios of water, ammonia, and carbonic acid, various intermediate salts will be formed containing mixtures or combinations of those mentioned above. Thus the ordinary commercial **carbonate of ammonia** is obtained by heating a mixture of chalk and either sulphate of ammonia (Chapter VI.) or sal-ammoniac: $2\text{NH}_4\text{Cl} + \text{CaCO}_3 = \text{CaCl}_2 + (\text{NH}_4)_2\text{CO}_3$. The normal salt, however, through loss of part of the ammonia, partly forms the acid salt, and, through loss of water, the carbamate, and most frequently presents the composition $\text{NH}_4\text{O}(\text{CONH}_2) + 2\text{OH}(\text{CO}_2\text{NH}_4) = 4\text{NH}_3 + 3\text{CO}_2 + 2\text{H}_2\text{O}$. This salt, in parting under various conditions with ammonia, carbonic anhydride, and water, does not present a constant composition, and ought rather to be regarded as a mixture of acid salt and amide salt. The latter must be recognised as entering into the composition of the ordinary carbonate of ammonia, because it contains less water than is required for the normal or acid salt;³⁵ but

³⁴ The acid salt, $(\text{NH}_4)\text{HCO}_3$, on losing water ought to form the *carbamic acid* $\text{OH}(\text{CNH}_2\text{O})$; but this is not formed, owing to the instability of the acid salt itself. Carbonic anhydride is given off and ammonia is produced, which gives ammonium carbamate.

³⁵ In the normal salt, $2\text{NH}_3 + \text{CO}_2 + \text{H}_2\text{O}$, in the acid salt, $\text{NH}_3 + \text{CO}_2 + \text{H}_2\text{O}$, in the carbamate, $2\text{NH}_3 + \text{CO}_2$, but in the commercial salt only $2\text{H}_2\text{O}$ to 3CO_2 .

on being dissolved in water this salt gives a mixture of acid and normal salts.

Each of the two ammoniacal salts of carbonic acid has its corresponding amide. That of the acid salt is OHCONH_2 , or **carbamic acid**. This acid is not known in a free state, but its corresponding ammoniacal salt or **ammonium carbamate** is known. The latter is easily and immediately formed by mixing 2 volumes of *dry* ammonia with 1 volume of dry carbonic anhydride, $2\text{NH}_3 + \text{CO}_2 = \text{NH}_4\text{O}(\text{CONH}_2)$; it is a solid substance, smells strongly of ammonia, attracts moisture from the air, and decomposes completely at 60° . The fact of this decomposition may be proved³⁶ by the density of its vapour, which is 13 ($\text{H}=1$); this exactly corresponds with the density of a mixture of 2 volumes of ammonia and 1 volume of carbonic anhydride. It is easily understood that such a combination will take place with any ammonium carbonate under the action of salts which take up the water—for instance, sodium or potassium carbonate³⁷—as in an anhydrous state ammonia and carbonic anhydride only form one compound, $\text{CO}_2, 2\text{NH}_3$.³⁸ As the normal ammonium carbonate contains two ammonias, and as the amides are formed with the separation of water at the expense of the hydrogen of the ammonias, so this salt has its symmetrical amide, $\text{CO}(\text{NH}_2)_2$. This must be termed **carbamide**. It is **identical with urea**, $\text{CN}_2\text{H}_4\text{O}$, which, contained in the urine (about 2 per cent. in human urine), is for the higher animals (especially the carnivora) the ordinary product of excretion³⁹ and oxidation of the nitrogenous substances found in the organism. If ammonium carbamate be heated to 140° (in a sealed tube, Bazaroff), or if carbonyl

³⁶ Naumann determined the following dissociation pressures of the vapour of ammonium carbamate (in millimetres of mercury):—

-10°	0°	$+10^\circ$	20°	30°	40°	50°	60°
5	12	30	62	124	248	470	770

With excess of either NH_3 or CO_2 (Horstmann and Isambert), the mass of the salt formed (in a solid state) increases and the vapour pressure decreases.

³⁷ Calcium chloride enters into double decomposition with ammonium carbamate. Acids (for instance, sulphuric) take up ammonia, and set free carbonic anhydride; whilst alkalies (such as potash) take up carbonic anhydride and set free ammonia, so that in this case only sodium or potassium carbonate can be used for removing water. An aqueous solution of ammonium carbamate does not entirely precipitate a solution of CaCl_2 , probably because calcium carbamate is soluble in water, and all the $(\text{NH}_3)_2\text{CO}_2$ is not converted, on dissolving, into the normal salt, $(\text{NH}_4\text{O})_2\text{CO}_2$.

³⁸ It must be imagined that the reaction takes place at first between equal volumes (Chap. VII.); but then carbamic acid, $\text{HO}(\text{CNH}_2\text{O})$, is produced, which, as an acid, immediately combines with the ammonia, forming $\text{NH}_4\text{O}(\text{CNH}_2\text{O})$.

³⁹ Urea is undoubtedly a product of the oxidation of the complex nitrogenous matters (albumin) of the animal body. It is found in the blood and is absorbed from the blood by the kidneys. A man excretes about 30 grams of urea per day. As a derivative of carbonic anhydride, urea is a product of oxidation just as CO_2 is.

chloride, COCl_2 , be treated with ammonia (Natanson), urea will be obtained, which shows its direct connection with carbonic acid—that is, the presence of carbonic acid and ammonia in it. From this it will be understood how, during the putrefaction of urine, urea is converted into ammonium carbonate: $\text{CN}_2\text{H}_4\text{O} + \text{H}_2\text{O} = \text{CO}_2 + 2\text{NH}_3$.

Thus urea, both by its origin and decomposition, is an amide of carbonic acid. Representing as it does ammonia (two molecules) in which hydrogen (two atoms) is replaced by the bivalent radicle of carbonic acid, urea retains the property of ammonia of entering into combination with acids (thus nitric acid forms $\text{CN}_2\text{H}_4\text{O}, \text{HNO}_3$), with bases (for instance, with mercuric oxide), and with salts (such as sodium chloride, ammonium chloride), but containing an acid residue it has no alkaline properties. It is soluble in water without change, but at a red heat loses ammonia and forms **cyanic acid**, CNHO , which is a nitrile of carbonic acid—that is to say, a cyanogen compound, corresponding to the acid ammonium carbonate, $\text{OH}(\text{CNH}_4\text{O}_2)$, which on parting with $2\text{H}_2\text{O}$ ought to form cyanic acid, CNOH . Liquid cyanic acid, exceedingly unstable at the ordinary temperatures, easily and frequently gives its stable solid polymeride, cyanuric acid, $\text{O}_3\text{H}_3\text{C}_3\text{N}_3$.^{39a} Both have the same composition, and they pass one into another at different temperatures. If crystals of cyanuric acid be heated to a temperature t° , then the vapour pressure, p , in millimetres of mercury (Troost and Hautefeuille) will be :

$t.$	160° ,	170° ,	200° ,	250° ,	300° ,	350°
$p.$	56,	68,	130,	220,	430,	1,200

The vapour contains cyanic acid, and, if it be *rapidly* cooled, it condenses into a mobile volatile liquid (specific gravity at $0^\circ = 1.14$). If the liquid cyanic acid be gradually heated, it passes into a new amorphous polymeride (cyamelide), which, on being heated, like cyanuric acid, forms vapours of cyanic acid. Hence, the above-mentioned figures give the pressure of dissociation of cyanuric acid, or the greatest pressure which the vapours of HOCN are able to attain at a given temperature, whilst at a greater pressure, or by the introduction of a larger mass of the substance into a given volume, the whole of the excess is converted into cyanuric acid. The properties of cyanic acid which we have described were observed principally by Wöhler, and clearly show the *faculty of polymerisation of cyanogen compounds*. This is observed in many other cyanogen derivatives, and is to be regarded as the consequence of the above-mentioned explanation of their nature. All cyanogen compounds are ammonium salts, $\text{R}(\text{CNH}_4\text{O}_2)$, deprived of

^{39a} Cyanic acid is a very unstable, readily changeable liquid, while cyanuric acid is a crystalline solid which is very stable at the ordinary temperature.

water, $2\text{H}_2\text{O}$; therefore the molecules, RCN , ought to possess the faculty of combining with two molecules of water or with other molecules in exchange for it (for instance, with H_2S , or HCl , or 2H_2 , &c.), and are therefore capable of combining together. The combination of molecules of the same kind to form more complex ones is what is meant by polymerisation.⁴⁰

Besides being a substance very prone to form polymerides, cyanic acid presents many other features of interest, expounded in greater detail in works on organic chemistry. However we may mention here the production of the cyanates by the oxidation of the metallic cyanides. Potassium cyanate, KCNO , is most often obtained in this way. Solutions of cyanates by the addition of sulphuric acid yield cyanic acid, which, however, immediately decomposes: $\text{CNHO} + \text{H}_2\text{O} = \text{CO}_2 + \text{NH}_3$. A solution of ammonium cyanate, $\text{CN}(\text{NH}_4)\text{O}$, behaves in the same manner, but only in the cold. On being heated it completely changes, as it is transformed into urea. The composition of the two substances is the same, namely, $\text{CN}_2\text{H}_4\text{O}$, but the structure, or the disposition of, and connection between, the elements, is different: in the ammonium cyanate one atom of nitrogen exists in the form of cyanogen, CN —that is, united with carbon—and the other as ammonium, NH_4 . The composition of this salt is best expressed by supposing one atom of the hydrogen in water to be replaced by ammonium and the other by cyanogen—i.e., that its composition is not symmetrical—whilst in urea both the nitrogen atoms are symmetrically and uniformly disposed as regards the radicle CO of carbonic acid: $\text{CO}(\text{NH}_2)_2$. For this reason, urea is much more stable than ammonium cyanate, and therefore the latter, on being slightly heated in solution, is converted into urea. This remarkable isomeric transformation was discovered by Wöhler in 1828 and formed an epoch in our science, being the first instance of the synthesis of an organic compound.⁴¹ Formamide, HCONH_2 , and **hydrocyanic acid**, HCN , as a nitrile, correspond with formic acid, HCOOH , and therefore ammonium formate, HCOONH_4 , and formamide, when acted on by heat and by substances which take up water

⁴⁰ Just as the aldehydes (such as $\text{C}_2\text{H}_4\text{O}$) are alcohols (like $\text{C}_2\text{H}_6\text{O}$) which have lost hydrogen and are also capable of entering into combination with many substances, and of polymerising, forming slightly volatile polymerides, which depolymerise on heating.

⁴¹ It has an important historical interest, more especially as at that time such an easy preparation of substances occurring in organisms without the aid of organic life was quite unexpected, for they were supposed to be formed under the influence of the forces acting in organisms, and without the latter their formation was considered impossible. And in addition to destroying this illusion, the easy transition of NH_4OCN into $\text{CO}(\text{NH}_2)_2$ is the best example of the passage of one system of equilibrium of atoms into another more stable system.

(phosphoric anhydride), form hydrocyanic acid, HCN, whilst, under many conditions (for instance, on combining with hydrochloric acid in presence of water), this hydrocyanic acid forms formic acid and ammonia. Although containing hydrogen in the presence of two acid-forming elements—namely, carbon and nitrogen⁴²—hydrocyanic acid does not give an acid reaction with litmus (cyanic acid has very marked acid properties); **but it forms salts, MCN**, thus presenting the properties of a feeble acid, and for this reason is called an **acid**. The small amount of energy which it has is shown by the fact that the cyanides of the alkali metals—for instance, potassium cyanide ($\text{KHO} + \text{HCN} = \text{H}_2\text{O} + \text{KCN}$) in solution—have a strongly alkaline reaction.⁴³ If ammonia be passed over charcoal at a red heat, especially in the presence of an alkali, or if gaseous nitrogen be passed through a mixture of charcoal and an alkali (especially potash, KHO), and also if a mixture of nitrogenous organic substances and alkali be heated to a red heat, the alkali metal combines with the carbon and nitrogen, forming a metallic cyanide, MCN—for example, KCN.^{43a} Potassium cyanide is much used in the arts, and is obtained, as above stated, under many circumstances—as, for instance, in iron smelting, especially with the assistance of wood charcoal, the ash of which contains much potash. The nitrogen of the air, the alkali of the ash, and the charcoal are brought into contact at a high temperature during iron smelting, and therefore, under these conditions, a considerable quantity of potassium cyanide

⁴² That ammonia and methane (marsh gas) do not show any acid properties is due to the presence of a large amount of hydrogen in both; but in hydrocyanic acid one atom of hydrogen is under the influence of two acid-forming elements. Acetylene, C_2H_2 , which contains but little hydrogen, presents acid properties in certain respects, for its hydrogen is replaced by metals. Hydrazoic acid, HN_3 , which contains little hydrogen also has the properties of an acid.

⁴³ Solutions of cyanides—for instance, those of potassium and barium—are decomposed by carbonic acid. Even the carbonic anhydride of the air acts in a similar way, and for this reason these solutions do not keep, because, in the first place, free hydrocyanic acid itself decomposes and polymerises, and, in the second place, with alkaline liquids it forms ammonia and formic acid. Hydrocyanic acid does not liberate carbonic anhydride from solutions of sodium or potassium carbonates. But a mixture of solutions of potassium carbonate and hydrocyanic acid yields carbonic anhydride on the addition of oxides like zinc oxide, mercuric oxide, &c. This is due to the great inclination which the cyanides exhibit of forming double salts. For instance, $\text{ZnK}_2(\text{CN})_4$ is formed, which is a soluble double salt.

^{43a} The conversion of the atmospheric nitrogen into cyanogen compounds, although possible, has not yet been carried out on a large scale, and one of the problems for future research should be the discovery of a practical and economical means of converting this nitrogen into metallic cyanides, not only because potassium cyanide has found an extensive and important use for the extraction of gold from even the poorest ores, but more especially because the cyanides furnish the means for effecting the synthesis of many complex carbon compounds, and the nitrogen contained in cyanogen passes easily into other forms of combination such as ammonia, which is of great importance in agriculture.

is formed. In practice it is not usual to prepare potassium cyanide directly, but a peculiar compound of it containing potassium, iron, and cyanogen. This compound is potassium ferrocyanide, and is also known as **yellow prussiate of potash**. This saline substance (see Chap. XXII.) has the composition $K_4FeC_6N_6 + 2H_2O$. The name of cyanogen (*κύανος*) is derived from the property which this yellow prussiate possesses of forming, with a solution of a ferric salt, FeX_3 , the familiar pigment, Prussian blue. The yellow prussiate is manufactured on a large scale, and is generally used as the source of the other cyanogen compounds.

If four parts of yellow prussiate are mixed with eight parts of water and three parts of sulphuric acid, and the mixture heated, it decomposes, volatile hydrocyanic acid separating. This was obtained for the first time by Scheele in 1782, but it was only known to him in solution. In 1809 Ittner prepared anhydrous prussic acid, and in 1815 Gay-Lussac finally settled its properties and showed that it contains only hydrogen, carbon, and nitrogen, CNH . If the distillate (a weak solution of HCN) be redistilled, and the first part collected, the anhydrous acid may be prepared from this stronger solution. In order to do this, pieces of calcium chloride are added to the concentrated solution, when the anhydrous acid floats as a separate layer, because it is not soluble in an aqueous solution of calcium chloride. If this layer be then distilled over a new portion of calcium chloride at the lowest temperature possible, the prussic acid may be obtained completely free from water. It is, however, necessary to use the greatest caution in work of this kind, because prussic acid, besides being extremely poisonous, is exceedingly volatile.⁴⁴ It is formed by the action of a silent electric discharge on a mixture of acetylene and nitrogen: $C_2H_2 + N_2 = 2CNH$.

⁴⁴ The mixture of the vapours of water and hydrocyanic acid, evolved on heating yellow prussiate with sulphuric acid, may be passed directly through vessels or tubes filled with calcium chloride. These tubes must be cooled, because, in the first place, hydrocyanic acid readily changes on being heated, and, in the second place, the calcium chloride, if warm, would absorb less water. The mixture of hydrocyanic acid and aqueous vapour on passing over a long layer of calcium chloride gives up water, and hydrocyanic acid alone remains in the vapour. It ought to be cooled as carefully as possible in order to bring it into a liquid condition. The method which Gay-Lussac employed for obtaining pure hydrocyanic acid consisted in the action of hydrochloric acid gas on mercuric cyanide. The latter may be obtained in a pure state if a solution of yellow prussiate be boiled with a solution of mercuric nitrate and the liquid filtered, and crystallised by cooling; the mercuric cyanide is then obtained in the form of colourless crystals, $Hg(CN)_2$.

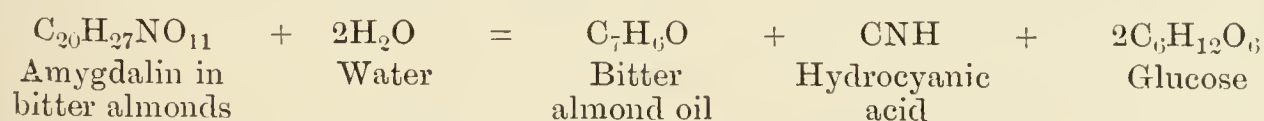
In order to obtain hydrocyanic acid in an anhydrous form, the decomposition of heated mercuric cyanide by hydrogen sulphide may be made use of. Here the sulphur and cyanogen change places, and hydrocyanic acid and mercuric sulphide are formed: $Hg(CN)_2 + H_2S = 2HCN + HgS$.

Anhydrous prussic acid is a very mobile and volatile liquid; its specific gravity is 0.697 at 18°; at lower temperatures, especially when mixed with a small quantity of water, it readily solidifies; it boils at 26°. ^{44a} It is soluble in all proportions in water, alcohol, or ether; weak aqueous solutions are used in medicine. ⁴⁵

The salts of potassium, sodium, ammonium, barium, calcium, and mercury are soluble in water, but the cyanides of manganese, zinc, lead, and many other metals are insoluble. They form double salts with potassium cyanide and similar metallic cyanides, an example of which we shall consider in a further description of the yellow prussiate. Not only are some of the double salts remarkable for their constancy and comparative stability, but so also are the soluble salt HgC_2N_2 , the insoluble silver cyanide AgCN , and even potassium cyanide in the absence of water. The last salt, ⁴⁶ when fused, acts as a reducing agent by means of the elements K and C, and oxidises when fused with lead oxide, forming potassium cyanate, KOCN , which establishes the connection between HCN and OHCN —that is, between the nitriles of formic and carbonic acids—and this connection is the same as that between the acids themselves, since formic acid, on oxidation, yields carbonic acid. Free cyanogen, $(\text{CN})_2$ or CNCN , corresponds with hydrocyanic acid in the same manner as free chlorine, Cl_2 or ClCl , corresponds with hydrochloric acid. This composition, judging from what has been already stated, exactly expresses that of the nitrile

^{44a} Weak solutions of peroxide of hydrogen may, it is said, be used as an antidote, because oxamide $(\text{CONOH})_2$ is formed by the action of H_2O_2 on HCN .

⁴⁵ A weak (up to 2 per cent.) aqueous solution of hydrocyanic acid is obtained by the distillation of certain vegetable substances. The so-called laurel water in particular enjoys considerable notoriety from its containing hydrocyanic acid. It is obtained by the steeping and distillation of laurel leaves. A similar kind of water is formed by the infusion and distillation of bitter almonds. It is well known that bitter almonds are poisonous, and have a peculiar bitter taste. This bitter taste is due to the presence of a certain substance called amygdalin, which can be extracted by alcohol. This amygdalin decomposes in an infusion of bruised almonds, forming the so-called bitter-almond oil, glucose, and hydrocyanic acid:



If an aqueous infusion of bitter almonds be distilled with water, the hydrocyanic acid and the volatile bitter almond oil are carried over with the aqueous vapour. The oil is insoluble in water, or only sparingly soluble, while the hydrocyanic acid remains as an aqueous solution. Bitter-almond water and laurel water are used in medicine, naturally only in small quantities, because any considerable amount has poisonous effects. Pure anhydrous hydrocyanic acid keeps without change, just like the weak solutions, but the strong solutions only keep in the presence of other acids. In the presence of many admixtures these solutions easily give a brown polymeric substance, which is also formed in a solution of potassium cyanide.

⁴⁶ This salt will be described in Chap. XIII.

of oxalic acid, and, as a matter of fact, oxalate of ammonia and the amide corresponding with it (oxamide, note 33), on being heated with phosphoric anhydride, which takes up the water, yield **cyanogen**, $(\text{CN})_2$. This substance is also produced by simply heating some of the metallic cyanides. Mercuric cyanide is particularly adapted for this purpose, because it is easily obtained in a pure state, and is then very stable. If mercuric cyanide be heated, it decomposes, in like manner to mercury oxide, into metallic mercury and cyanogen: $\text{HgC}_2\text{N}_2 = \text{Hg} + \text{C}_2\text{N}_2$.⁴⁷ When cyanogen is formed, part of it always polymerises into a dark brown insoluble substance called **paracyanogen**, capable of forming cyanogen when heated to redness.⁴⁸ Cyanogen is a colourless, poisonous gas, with a peculiar smell, and is easily condensed, by cooling, into a colourless liquid, insoluble in water and having a specific gravity of 0.86. It boils at about -21° , and therefore cyanogen may be easily condensed into a liquid by a strong freezing mixture. At -35° liquid cyanogen solidifies. The gas is soluble in water and in alcohol to a considerable extent—namely, 1 volume of water absorbs as much as $4\frac{1}{2}$ volumes, and 1 of alcohol 23 volumes. Cyanogen resists the action of a tolerably high temperature without decomposing, but under the action of the electric spark the carbon is separated, leaving a volume of nitrogen equal to the volume of the gas taken. As it contains carbon it burns, and the colour of the flame is reddish-violet, owing to the presence of nitrogen, all compounds of which impart more or less of this reddish-violet hue to the flame. During the combustion of

⁴⁷ For the preparation it is necessary to take completely dry mercuric cyanide, because when heated in the presence of moisture it gives ammonia, carbonic anhydride, and hydrocyanic acid. Instead of mercuric cyanide, a mixture of perfectly dry yellow prussiate and mercuric chloride may be used, double decomposition and the formation of mercuric cyanide then taking place in the retort. Silver cyanide also disengages cyanogen, on being heated.

⁴⁸ **Paracyanogen** is a brown substance (having the composition of cyanogen) which is formed during the preparation of cyanogen by all methods, and remains as a residue. Silver cyanide, on being slightly heated, fuses, and on being further heated evolves cyanogen, a considerable quantity of paracyanogen remaining in the residue. It is remarkable that here exactly half the cyanogen becomes gaseous, and the other half is transformed into paracyanogen. Metallic silver will be found in the residue with the paracyanogen; it may be extracted with mercury or nitric acid, which does not act on paracyanogen. If paracyanogen is heated in a vacuum it dissociates, forming cyanogen; Troost and Hautefeuille (1868) found the **dissociation pressures** at different temperatures to be—

$t = 530^\circ$	581°	600°	635°
$p = 90$	143	296	1,089 mm.

However, even at 550° , part of the cyanogen decomposes into carbon and nitrogen. The reverse transition of cyanogen into paracyanogen commences at 350° , and at 600° proceeds rapidly. And if the transition of the first kind is likened to evaporation, then the reverse transition, or polymerisation, presents a likeness to the transformation of vapours into the solid state.

cyanogen, carbonic anhydride and nitrogen are formed. The same products are obtained in the eudiometer with oxygen or by the action of cyanogen on many oxides at a red heat.

The relation of cyanogen to the metallic cyanides is seen not only in the fact that it is formed from mercuric cyanide, but also by the formation of cyanide of sodium or potassium when it is heated with either of those metals, the sodium or potassium taking fire in the cyanogen. When a mixture of hydrogen and cyanogen is heated to 500° (Berthelot),⁴⁹ or exposed to the action of the silent discharge (Boillot), hydrocyanic acid is formed, so that the reciprocity of the transitions leaves no doubt that all the nitriles of the organic acids contain cyanogen, just as all the organic acids contain carboxyl and in it the elements of carbonic anhydride. Besides the amides, the nitriles (or cyanogen compounds, RCN), and nitro-compounds (containing the radicle of nitric acid, RNO_2), there are a great number of other substances containing at the same time carbon and nitrogen, particulars of which must be sought for in special works on organic chemistry.

⁴⁹ Cyanogen (like chlorine) is absorbed by a solution of sodium hydroxide, sodium cyanide and cyanate being produced: $\text{C}_2\text{N}_2 + 2\text{NaHO} = \text{NaCN} + \text{CNNaO} + \text{H}_2\text{O}$. But the latter salt decomposes relatively easily, and moreover part of the cyanogen liberated by heat from its compounds undergoes a more complex transformation.

CHAPTER X

SODIUM CHLORIDE—BERTHOLLET'S LAWS—HYDROCHLORIC ACID

IN the preceding chapters we have become acquainted with the most important properties of the four elements, hydrogen, oxygen, nitrogen, and carbon. They are sometimes termed the **organogens**, because they enter into the composition of organic substances. Their mutual combinations may serve as types for all others—that is, they present types (forms) of the combinations in which the other elements also combine together.

Hydrogen,	HH,	or, in general,	HR.
Water,	H ₂ O,	„ „	H ₂ R.
Ammonia,	H ₃ N,	„ „	H ₃ R.
Marsh gas,	H ₄ C,	„ „	H ₄ R.

One, two, three, and four atoms of hydrogen enter into these molecules for one atom of another element. No compounds of one atom of oxygen with three or four atoms of hydrogen are known; hence the atom of oxygen does not possess certain properties which are found in the atoms of carbon and nitrogen.

The power of an element to form a compound of definite composition with hydrogen, as we have already seen, gives the possibility of foretelling the composition of many others of its compounds. Thus, if we know that an element, M, combines with hydrogen, forming only HM, but not forming H₂M, H₃M, &c., then we must conclude, on the basis of the law of substitution, that this element will give compounds M₂O, M₃N, MHO, MH₃C, &c. Chlorine is an example of this kind. If we know that another element, R, like oxygen, gives with hydrogen a molecule H₂R, then we may expect that it will form compounds similar to hydrogen peroxide, the metallic oxides, carbonic anhydride or carbonic oxide, and others. Sulphur is an instance of this kind. Hence the elements may be classified according to their resemblance to hydrogen, oxygen, nitrogen, and carbon, and in conformity with this analogy it is possible to foretell, if not the properties (for example, the

acidity or basicity), at any rate the composition,¹ of many of their compounds. This forms the substance of **the conception of the valency or atomicity of the elements**. Hydrogen is taken as the representative of the univalent elements, giving compounds RH , $R(OH)$, R_2O , RCl , R_3N , R_4C , &c. Oxygen, in that form in which it gives water, is the representative of the bivalent elements, forming RH_2 , RO , RCl_2 , $RHCl$, $R(OH)_2$, R_2C , RCN , &c. In carbon are exemplified the properties of the quadrivalent elements, forming RH_4 , RO_2 , $RO(OH)_2$, $R(OH)_4$, RHN , RCl_4 , $RHCl_3$, &c. We meet with these **forms of combination**, or degrees of union of atoms, in all other elements, some being analogous to hydrogen, others to oxygen,

¹ But it is impossible to foretell all the compounds formed by an element from its atomicity or valency, because the atomicity of the elements is variable. In CO_2 , COX_2 , CH_4 , and the multitude of carbon compounds corresponding with them, the carbon C is quadrivalent, but in CO either the carbon must be taken as bivalent or the atomicity of oxygen be regarded as variable. Moreover, carbon is an example of an element which preserves its atomicity to a greater degree than most of the other elements. Nitrogen in NH_3 , $NH_2(OH)$, N_2O_3 , and even in CNH , must be considered as trivalent, but in NH_4Cl , $NO_2(OH)$, and in all their corresponding compounds it is necessarily pentavalent. In N_2O , if the atomicity of oxygen is 2, nitrogen has an uneven atomicity (1, 3, 5), whilst in NO it is bivalent. If sulphur be bivalent, like oxygen, in many of its compounds (for example, H_2S , SCl_2 , KHS , &c.), then it could not be foreseen from this that it would form SO_2 , SO_3 , SCl_4 , $SOCl_2$, and a series of similar compounds in which its atomicity must be acknowledged as greater than 2. Thus SO_2 , sulphurous anhydride, has many points in common with CO_2 , and if carbon be quadrivalent then the S in SO_2 is quadrivalent. Therefore the principle of atomicity (valency) of the elements cannot be considered established as the basis for the study of the elements, although it gives an easy method of grasping many analogies. I consider the four following as the chief obstacles to acknowledging the atomicity of the elements as a primary conception for the consideration of the properties of the elements: 1. Such univalent elements as H, Cl, &c., appear in a free state as molecules H_2 , Cl_2 , &c., while others, e.g., K, Na, contain only one atom in the molecule in a free state. Hence it follows that *free affinities* may exist. Granting this, nothing prevents the assumption that free affinities exist in all unsaturated compounds; for example, we might consider nitrogen as pentavalent in NH_3 with two free affinities. If such instances of free affinities be admitted, then all the possible advantages to be gained by the application of the doctrine of atomicity (valency) are lost. 2. There are instances—for example, ICl_3 , $KICl_4$ (Chap. IV., note 3), &c.—where univalent elements are combined in molecules which are more complex than R_2 , and form molecules, R_3 , &c.; this necessitates the primary univalent elements being considered as variable in their atomicity. 3. The periodic system of the elements, with which we shall afterwards become acquainted, shows that there is a law or rule for the variation of the forms of oxygen and hydrogen compounds; chlorine is univalent with respect to hydrogen, and septavalent with respect to oxygen; sulphur is bivalent towards hydrogen, and sexavalent as regards oxygen; phosphorus is trivalent to hydrogen and pentavalent in respect to oxygen—the sum is in every case being equal to 8. Hence the power of the elements to change their atomicity is an essential part of their nature, so that constant valency cannot be considered as a fundamental property. 4. Crystallohydrates (for instance, $NaCl \cdot 2H_2O$, or $NaBr \cdot 2H_2O$), double salts (such as $PtCl_4 \cdot 2KCl$, H_2SiF_6 , &c.) and similar complex compounds (and, according to Chap. I., solutions also) demonstrate the capacity not only of the elements themselves, but also of their saturated and limiting compounds, of entering into further combinations.

and others to nitrogen or to carbon. But besides these quantitative analogies or resemblances, there exist among the elements qualitative analogies and relations which are not fully seen in the compounds of the elements which have been considered, but are most distinctly exhibited in the formation of bases, acids, and salts of different types and properties. Therefore, for a complete study of the elements and their compounds it is especially important to become closely acquainted with the salts, as substances of a peculiar character, and with the corresponding acids and bases. Common table salt, or sodium chloride, NaCl , may in every respect be taken as a type of salts in general, and we will therefore pass to the consideration of this substance (and of hydrochloric acid and the base sodium hydroxide corresponding with it) formed by the non-metal chlorine and the metal sodium.

Sodium chloride, NaCl , the familiar table salt, occurs, although in very small quantities, in all the primary formations of the earth's crust,² from which it is washed away by the atmospheric waters; it is contained in small quantities in all flowing waters, and is in this manner conveyed to the oceans and seas. The immense mass of salt in the ocean has been accumulated by this process which has been carried on from the remote ages of the earth's creation, because the water has evaporated from them while the salt has remained in solution. The salt of sea water serves as the source not only for its direct extraction, but also for the formation of other masses of workable salt, such as rock salt, and of saline springs and lakes.^{2a}

The extraction of salt **from sea water** is carried on in several ways. In southern climes, especially on the shores of the Atlantic Ocean and the Mediterranean and Black Seas, the summer heats are taken advantage of. A convenient low-lying sea shore is chosen, and a

² The primary formations are those which do not bear any distinct traces of having been deposited from water (have not a stratified formation and contain no remains of animal or vegetable life), occur under the sedimentary formations of the earth, and are everywhere uniform in composition and structure, the latter being generally distinctly crystalline. If it be assumed that the earth was originally in a molten condition, the first primary formations formed the first solid crust of the earth. It is from the products of decomposition (mostly by atmospheric, aqueous, and organic agencies, &c.), that all the rocks and substances of the earth's surface have arisen. In speaking of the origin of one or another substance, we can only, on the basis of facts, descend to the primary formations, of which granite, gneiss, and trachyte may be taken as examples.

^{2a} Chloride of sodium has been found to occur in the atmosphere in the form of a fine dust; in the lower strata it is present in larger quantities than in the upper, so that the rain water falling on mountains contains less NaCl than that falling in valleys. Müntz (1891) found that a litre of rain water collected on the summit of the Pic du Midi (2,877 metres above the sea level) contained 0.34 milligram of chloride of sodium, while a litre of rain collected from the valley contained 2.5–7.6 milligrams.

whole series of basins, communicating with each other, are constructed along it. The upper of these basins are filled with sea water by pumping, or else advantage is taken of high tides. These basins are sometimes separated from the sea by natural sand-banks (limans) or by artificial means, and in spring the water already begins to evaporate considerably. As the solution becomes more concentrated, it is run into the succeeding basins, and the upper ones are supplied with a fresh quantity of sea water, or else an arrangement is made enabling the salt water to flow gradually through the series of basins. It is evident that the beds of the basins should be as far as possible impervious to water, and for this purpose they are made of beaten clay. Crystals of salt begin to separate out when the concentration attains 28 per cent. of salt (which corresponds to 28° of Baumé's hydrometer). These are raked off, and employed for all those purposes to which table salt is applicable. In the majority of cases only the first half of the sodium chloride which can be separated from the sea water is extracted, because the second half has a bitter taste owing to the presence of magnesium salts which separate out together with the sodium salt. But in certain localities—as, for instance, in the estuary of the Rhone, on the island of Camarga³—the evaporation is carried on to the very end, in order to obtain those magnesium and potassium salts which separate out at the end of the evaporation of sea water. From 100 parts of sea water there separates out (by natural and artificial evaporation) at the very commencement of the operation, about one part of tolerably pure table salt, the total amount held in solution being about $2\frac{1}{2}$ per cent. The remaining portion separates out intermixed with the bitter salts of magnesium, which, owing to their solubility and the small amount in which they are present (less than 1 per cent.), only separate out in traces in the first crystallisations. A certain amount of gypsum, or calcium sulphate, $\text{CaSO}_4, 2\text{H}_2\text{O}$, separates together with or even before the table salt. On still further evaporation (after the separation of NaCl with MgSO_4) the chlorides of potassium and magnesium begin to separate in a state of combination, forming the double salt $\text{KMgCl}_3, 6\text{H}_2\text{O}$, which occurs in nature as **carnallite**.⁴ After the separation of this salt from sea water, there

³ The extraction of the potassium salts (or so-called summer salts) was carried on at the isle of Camarga (at the mouth of the Rhone) about 1870, when I had occasion to visit that spot. At the present time the deposits of Stassfurt provide a much cheaper salt, owing to the evaporation and separation of the salt being carried on there by natural means and requiring only such treatment and refining as are also necessary for the 'summer salt' obtained from sea water. The Stassfurt deposits present a most wonderful instance of industrial activity.

⁴ The double salt $\text{KCl}, \text{MgCl}_2$ is a crystallohydrate of KCl and MgCl_2 , and is only

remains a mother liquor containing a large amount of magnesium chloride in admixture with various other salts.⁵ The extraction of sea salt is usually carried on for the purpose of procuring table salt, and therefore directly it begins to separate mixed with a considerable proportion ⁶ of magnesium salts the remaining liquor is run back into the sea.

The same process as is employed for artificially obtaining salt in a crystalline form from sea water has been repeatedly accomplished on a gigantic scale during the geological evolution of the earth; upheavals of the earth have cut off portions of the sea from the remainder (the Dead Sea being formerly a part of the Mediterranean, and the Sea of Aral of the Caspian), and their water has evaporated and formed (if the mass of the inflowing fresh water were less than that of the mass evaporated) deposits of **rock salt**. It is always accompanied by gypsum, because the latter is separated from sea water with or before the sodium chloride. For this reason rock salt may always be looked for in those localities where there are deposits of gypsum. But inasmuch as the gypsum remains on the spot where it has been deposited (as it is a sparingly soluble salt), whilst the rock salt (as one which is very soluble) may be washed away by rain or fresh running water, it may sometimes happen that although gypsum is still found there may be no salt; but, on the other hand, where there is rock salt there will always be gypsum. As the geological changes of the earth's surface are still proceeding at the present day, so in the midst of the dry land salt lakes are met with, which are sometimes scattered over vast districts formerly covered by seas now dried up. Such is the

formed from solutions containing an excess of magnesium chloride, because water decomposes this double salt, extracting the more soluble magnesium chloride from it. Van't Hoff studied all the conditions (temperatures), indicating the relative amounts of KCl, MgCl₂, and H₂O, which lead to the formation of carnallite.

⁵ Owing to the fundamental property of salts of interchanging their metals, it cannot be said that sea water contains this or that salt, but only that it contains definite amounts of certain metals M (univalent like Na and K, and bivalent like Mg and Ca), and haloids X (univalent like Cl, Br, and bivalent like SO₄, CO₃), which are disposed in every possible kind of grouping; for instance, K as KCl, KBr, K₂SO₄, Mg as MgCl₂, MgBr₂, MgSO₄, and so on for all the other metals. On evaporation different salts separate out consecutively only as they reach saturation. A proof of this may be seen in the fact that a solution of a mixture of sodium chloride and magnesium sulphate (both of which salts are obtained from sea water, as was mentioned above), when evaporated, deposits crystals of these salts, but when refrigerated (if the solution be sufficiently saturated) the salt Na₂SO₄·10H₂O is first deposited because it is the first to arrive at saturation at low temperatures. Consequently this solution contains MgCl₂ and Na₂SO₄, besides MgSO₄ and NaCl. So it is with sea water.

⁶ The salt extracted from water is piled up in heaps and left exposed to the action of rain water, which purifies it, as the water becomes saturated with sodium chloride and then no longer dissolves it, but washes out the impurities.

origin of the salt deposited in the Karabuga Bay of the Caspian Sea, and of many of the salt lakes about the lower portions of the Volga and in the Kirghiz steppes, where at a geological epoch preceding the present the Aralo-Caspian Sea extended. Such are the Baskunchaksky (in the Government of Astrakhan, 112 square kilometres superficial area), the Eltonsky (140 versts from the left bank of the Volga, and 200 square kilometres in superficial area), and upwards of 700 other salt lakes lying about the lower portions of the Volga. In those in which the annual inflow of fresh water is less than that evaporated yearly, and in which the concentration of the solution has reached saturation, the **self-deposited** salt is found already deposited on their beds, or is being yearly deposited during the summer months. Certain limans, or seaside lakes, of the Azoff Sea are essentially of the same character—as, for instance, those in the neighbourhood of Henichesk and Berdiansk. The saline soils of certain Central Asian steppes, which suffer from a want of atmospheric fresh water, have a similar origin. Their salt originally proceeded from seas previously covering these localities, and has not yet been washed away by fresh water. The main result of the above-described process of nature is the formation of masses of rock salt, which are, however, being gradually washed away by the subsoil waters flowing in their neighbourhood, and afterwards rising to the surface in certain places as **saline springs**, which indicate the presence of masses of deposited **rock salt** in the depths of the earth. If the subsoil water flows along a stratum of salt for a sufficient length of time it becomes saturated; but in flowing, in its further course, along an impervious stratum (clay) it becomes diluted by the fresh water leaking through the upper soil, and therefore the greater the distance of a saline spring from the deposit of rock salt, the poorer will it be in salt. A perfectly saturated brine, however, may be procured from the depths of the earth by means of bore-holes. The deposits of rock salt themselves, which are sometimes hidden at great depths below the earth's strata, may be discovered by the guidance of bore-holes and of the direction of the strata of the district. Deposits of rock salt, about 35 metres thick and 20 metres below the surface, were discovered in this manner in the neighbourhood of Brianstcheffky and Dekonoffky, in the Bakhmut district of the Government of Ekaterinoslav. Large quantities of most excellent rock salt are now (since 1880) obtained from these deposits, the presence of which was indicated by the neighbouring salt springs (near Slaviansk and Bakhmut) and by bore-holes which had been sunk in these localities for procuring strong (saturated) brines. The Stassfurt deposits of rock salt near Magdeburg in Germany are celebrated for their many remarkable

peculiarities.⁷ The plentiful distribution of saline springs in this and the neighbouring districts suggested the presence of deposits of rock salt in the vicinity. Deep bore-holes sunk in this locality did in fact give a richer brine—even quite saturated with salt. On sinking to a still greater depth, the deposits of salt themselves were at last arrived at. But the first deposit which was met with consisted of a bitter salt unfit for consumption, and was therefore called refuse salt (*Abraumsalz*). On sinking still deeper vast beds of real rock salt were struck. In this instance the presence of these upper strata containing salts of potassium, magnesium, and sodium is an excellent proof of the formation of rock salt from sea water. It is very evident that not only a case of evaporation to the end—as far, for instance, as the separation of carnallite—but also the preservation of such soluble salts as separate out from sea water after the sodium chloride, must be a very exceptional phenomenon, which is not repeated in all deposits of rock salt. The Stassfurt deposits form a rich source of potassium salts which have many practical uses.^{7a}

A saturated brine, formed by the continued contact of subsoil water with rock salt, is extracted by means of bore-holes, as, for instance, in the Governments of Perm, Kharkoff, and Ekaterinoslav. Sometimes, as at Berchtesgaden (and at Hallein) in Austria, spring water is run on to underground beds of rock salt containing much clay.

If a saline spring, or the salt water pumped from bore-holes, contains but little salt, then the first concentration of the natural solution is not carried on by the costly consumption of fuel, but by the cheaper method of evaporation by means of the wind. For this purpose

⁷ When the German savants pointed out the exact locality of the Stassfurt salt-beds and their depth below the surface, on the basis of information collected from various quarters respecting bore-holes and the direction of the strata, and when the borings, conducted by the Government, struck a salt-bed which was bitter and unfit for use, there was a great outcry against science, and the doubtful result even caused the cessation of the further work of deepening the shafts. It required a great effort to persuade the Government to continue the work. Now, when the pure salt encountered below forms one of the important riches of Germany, and when those 'refuse salts' have proved to be most valuable (as a source of potassium and magnesium), we should see in the utilisation of the Stassfurt deposits one of the conquests of science for the common welfare.

^{7a} In Western Europe, deposits of rock salt have long been known at Wieliczka, near Cracow, and at Cardona in Spain. In Russia the following deposits are known: (a) the vast masses of rock salt (3 square kilometres area and up to 140 metres thick) lying directly on the surface of the earth at Iletzky Zastchit, on the left bank of the river Ural, in the Government of Orenburg; (b) the Chingaksky deposit, 90 versts from the river Volga, in the Enotaeffsky district of the Government of Astrakhan; (c) the Kulepinsky deposits (whose thickness attains 150 metres), on the Araks, in the Government of Erivan in the Caucasus; (d) the Katchiezmansky deposit in the province of Kars; (e) the Krasnovodsky deposit in the Trans-Caspian province.

so-called *graduators* are constructed; these consist of long sheds, which are sometimes several versts long, and extend in a direction at right angles to that of the usual course of the wind in the district. The sheds are open at the sides, and are filled with brushwood, as shown in fig. 73. Troughs, AB, CD, into which the salt water is pumped, run along the top. On flowing through the openings, *a*, the water spreads over the brushwood and presents a very large surface for evaporation, in conse-

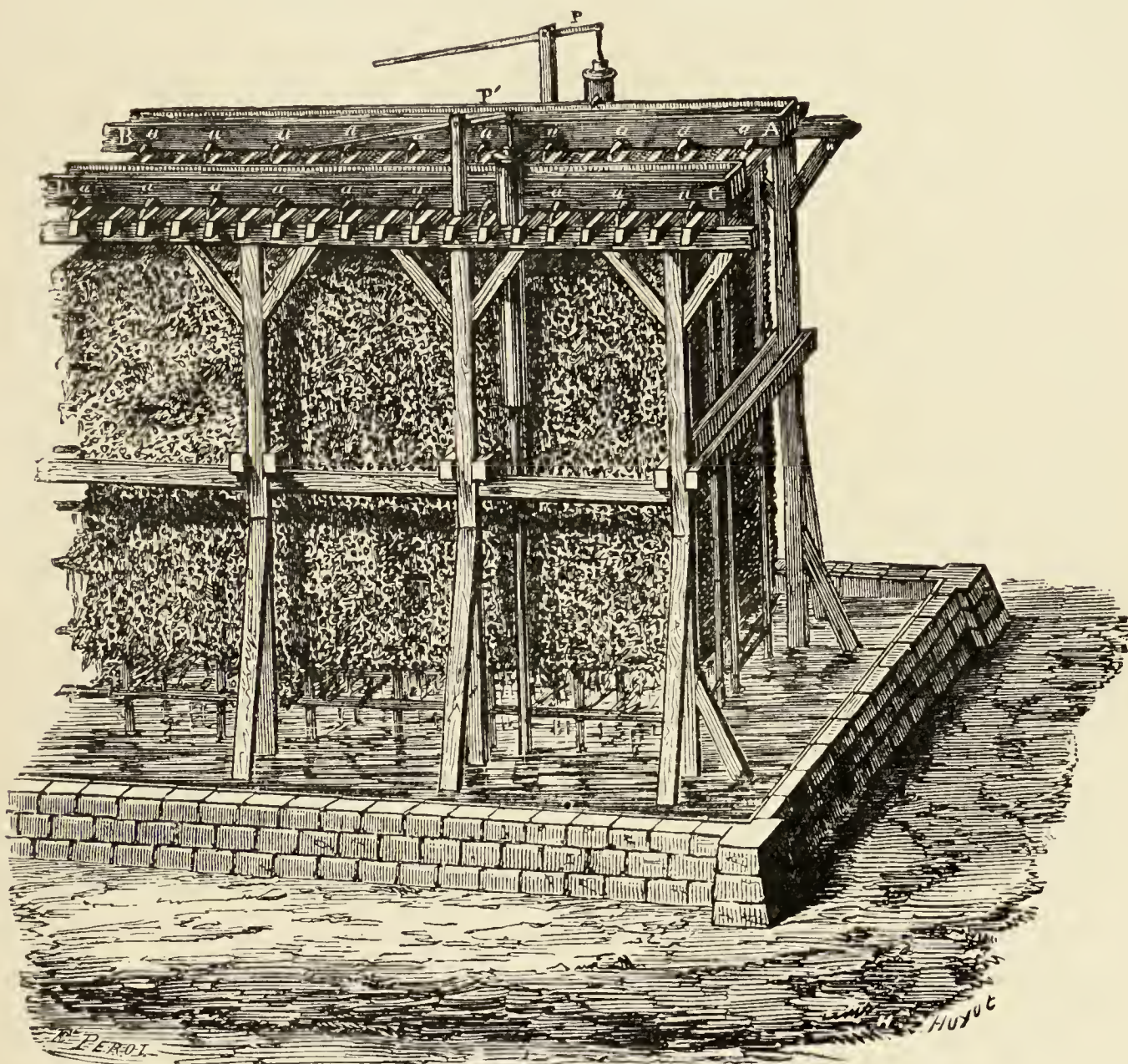


FIG. 73.—Graduator for the evaporation of the water of saline springs.

quence of which it rapidly becomes concentrated in warm or windy weather. After trickling over the brushwood, the solution is pumped up by the pumps *P P'*, and run a second and a third time through the graduator, until it reaches a concentration of 12 to 15 parts of salt in 100 parts of solution. Strong natural solutions of salt, and also the graduated solutions, are evaporated in large shallow metallic vessels, which are either heated by the direct action of the flame from below or from above. These vessels are made of boiler plate, and are called

salt-pans. The first portions of the salt crystallising out in the salt-pans are invariably contaminated with gypsum, but the portions separating later are distinguished by their purity. Since it has become possible to discover the saline deposits themselves, the extraction of table salt from saline springs has fallen somewhat into disuse, and is only able to hold its ground in places where fuel is cheap.

On the average, 20 lb. of table salt are consumed yearly per head of population, either directly in food or for cattle. In those countries where common salt is employed in technical processes, and especially in England, almost an equal quantity is consumed in the production of substances containing chlorine and sodium, and especially in the manufacture of washing soda, &c., and of chlorine compounds (bleaching powder and hydrochloric acid). The yearly production of salt on the globe amounts to ten million tons.

Although certain lumps of rock salt and crystals of bay salt sometimes consist of almost pure sodium chloride, yet the ordinary commercial salt contains various impurities, the most common of which are magnesium salts. If the salt is pure, its solution gives no precipitate with sodium carbonate, Na_2CO_3 , showing the absence of magnesium salts, because magnesium carbonate, MgCO_3 , is insoluble in water.⁸ For ordinary use the bulk of the salt obtained can be employed directly without further purification; but some salts are purified by solution and crystallisation of the solution after standing, in which case the evaporation is not carried on to dryness, and the impurities remain in the *mother liquor* or in the sediment. When perfectly pure salt is required for chemical purposes it is best obtained as follows: A saturated solution of table salt is prepared, and hydrochloric acid gas is passed through it; this precipitates the sodium chloride (which is not soluble in a strong solution of hydrochloric acid), whilst the impurities remain in solution. By repeating the operation and fusing the salt (when adhering hydrochloric acid is volatilised) a pure salt is obtained, which is again crystallised from its solution by evaporation.⁹

Pure sodium chloride, in well-defined crystals (slowly deposited at the bottom of the liquid), is a colourless and transparent substance

⁸ The fracture of rock salt generally shows the presence of interlayers of impurities which are sometimes very small in weight, but visible owing to their different refraction. In the excellently laid-out salt mines of Briansk I counted (1888) on an average ten interlayers per metre of thickness, and between these the salt was in general very pure, and in places quite transparent. If this be the case, then for the whole thickness (about 35 metres) of the bed there would be 350 interlayers. These probably correspond with the yearly deposition of the salt. In this case the deposition would have extended over more than 300 years.

⁹ My own investigations have shown that not only the sulphates, but also the potassium salts, are entirely removed by this method.

resembling glass, but brittle and fragile.¹⁰ Common salt always crystallises in the cubic system, most frequently in **cubes**, and more rarely in octahedra. Large transparent cubes having edges up to 10 centimetres long are sometimes found in masses of rock salt.¹¹ When evaporated in the open the salt often separates out on the surface¹² as cubes, which grow on to each other in the form of square pyramidal funnels. In still weather, these clusters are able to support themselves on the surface of the water for a long time, and sometimes go on increasing to a considerable extent, but they sink directly the water penetrates to their interior. Salt fuses to a colourless liquid (sp. gr. 1.602, according to Quincke) at 851° (V. Meyer); if pure it solidifies to a non-crystalline mass, and if impure to an opaque mass having a rough surface. In fusing, sodium chloride commences to volatilise (its weight decreases) and at a white heat it vaporises completely and with great ease, but at the ordinary temperature it may, like all ordinary salts, be considered as non-volatile, although as yet no exact experiments have been made in this direction.

¹⁰ According to the determinations of Klodt, the Briansk rock salt withstands a pressure of 340 kilograms per square centimetre, whilst glass withstands 1,700 kilos. In this respect salt is twice as secure as bricks, and therefore immense masses may be extracted from underground workings with perfect safety, without having recourse to brickwork supports, merely taking advantage of the properties of the salt itself.

¹¹ To obtain well-formed crystals, a saturated solution is mixed with ferric chloride, several small crystals of sodium chloride being placed at the bottom, and the solution then allowed to evaporate slowly in a vessel with a loose-fitting cover. Octahedral crystals are obtained by the addition of borax, urea, &c. to the solution. Very fine crystals are formed in a mass of gelatinous silica.

¹² If a solution of sodium chloride be slowly heated from above, where the evaporation takes place, then the upper layer will become saturated before the lower and cooler layers, and therefore crystallisation will begin on the surface, and the crystals first formed will float—having also dried from above—on the surface until they become quite soaked. Being heavier than the solution the crystals are partially immersed in it, and the following crystallisation, also proceeding on the surface, will only form crystals by the side of the original crystals. A funnel is formed in this manner. It will be borne on the surface like a boat (if the liquid be quiescent), because it will grow more from the upper edges. We can thus understand this, at first sight, strange funnel form of crystallised salt. To explain why the crystallisation under the above conditions begins at the surface and not at the lower layers, it must be mentioned that the specific gravity of a crystal of sodium chloride is 2.16, and that a solution saturated at 25° contains 26.7 per cent. of salt and has a sp. gr. 1.2004 at 25°/4°; at 15° a saturated solution contains 26.5 per cent. of salt and has a sp. gr. 1.203 at 15°/4°. Hence a solution saturated at a higher temperature is specifically lighter, notwithstanding the greater amount of salt it contains. With many substances *surface crystallisation* cannot take place, because their solubility increases more rapidly with the temperature than their specific gravity decreases. In this case the saturated solution will always be in the lower layers, where also the crystallisation will take place. Besides which it may be added that as a consequence of the properties of water and solutions, when they are heated from above (for instance, by the sun's rays) the warmer layers, being the lightest, remain above, whilst when heated from below they rise to the top.

A saturated ¹³ solution of table salt (containing 26·4 per cent.) has at the ordinary temperature a specific gravity of about 1·2. The specific gravity of the crystals is 2·167 (17°). The salt which separates out at the ordinary and higher temperatures contains no water of crystallisation; ¹⁴ but if the crystals are formed at a low temperature, especially from a saturated solution cooled to -12° , they then present a prismatic form, and contain two equivalents of water, $\text{NaCl}\cdot 2\text{H}_2\text{O}$. At the ordinary temperature these crystals split up into sodium chloride and its solution.¹⁵ Unsaturated solutions of table salt when cooled below 0° give ¹⁶ crystals of ice, but when the solution has a com-

¹³ By combining the results of Poggiale, Müller, and Karsten, we find that a saturated solution at t° , from 0° to 108° , contains $35\cdot7 + 0\cdot024t + 0\cdot0002t^2$ grams of salt per 100 grams of water. But I think that at low temperatures (for instance, -15°) the solubility will be different, because $\text{NaCl}\cdot 2\text{H}_2\text{O}$ is then formed. Perfect confidence cannot be placed in the figures.

¹⁴ Perfectly pure *fused* salt is not hygroscopic, according to Karsten, whilst the crystallised salt, even when quite pure, attracts as much as 0·6 per cent. of water from moist air, according to Stas.

If the salt contains impurities—such as magnesium sulphate, &c.—it is more hygroscopic. If it contains any magnesium chloride, it partially deliquesces in a damp atmosphere. The crystallised and not perfectly pure salt decrepitates when heated, owing to its containing water. The pure salt, and also the transparent rock salt, or that which has been once fused, does not decrepitate. Fused sodium chloride shows a faint alkaline reaction to litmus, which has been noticed by many observers, and is due to the presence of sodium oxide (probably formed by the action of the oxygen of the atmosphere). According to A. Stcherbakoff very sensitive litmus (washed in alcohol and neutralised with oxalic acid) shows a faint alkaline reaction even with the crystallised salt.

From the fact that the action of Na upon molten NaCl gives a blue coloration, and apparently leads to the formation of a lower state of combination, Na_2Cl , which dissolves in water giving NaHO, it may be gathered that the native salt also contains traces of this compound, particularly as pieces of rock salt of a blue tint are sometimes met with.

It may be observed that rock salt sometimes contains cavities filled with a colourless liquid. Certain kinds of rock salt emit an odour like that of hydrocarbons. These phenomena have as yet received very little attention.

¹⁵ By cooling a solution of table salt saturated at the ordinary temperature to -15° , I obtained, first of all, well-formed tabular (six-sided) crystals, which when warmed to the ordinary temperature disintegrated (with the separation of anhydrous sodium chloride), and later prismatic needles up to 20 mm. long were formed from the same solution. I have not yet investigated the reason of the difference in crystalline form.

¹⁶ Notwithstanding the great simplicity (Chap. I., note 49) of the observations on the formation of ice from solution, still, even for sodium chloride they cannot yet be considered as sufficiently harmonious. According to Blagden and Raoult, the temperature of the formation of ice from a solution containing c grams of salt per 100 grams of water is $-0\cdot6c^{\circ}$ to $c=10$; according to Rosetti, $-0\cdot649c^{\circ}$ to $c=8\cdot7$; according to De Coppet (to $c=10$), $-0\cdot55c - 0\cdot006c^2$, and according to Karsten (to $c=10$) $-0\cdot762c + 0\cdot0084c^2$, whilst Guthrie gives a much lower figure.

The data for strong solutions are not less contradictory. Thus with 20 per cent. of salt, ice is formed at $-14\cdot4^{\circ}$ according to Karsten, at -17° according to Guthrie, and at

position of nearly $\text{NaCl}, 10\text{H}_2\text{O}$ it solidifies completely at a temperature of about -23° . A solution of table salt saturated at its boiling-point boils at about 109° , and contains about 42 parts of salt per 100 parts of water.

Of all their physical properties the specific gravity of solutions of sodium chloride is the one which has been the most fully investigated. A comparison of all the existing determinations of the specific gravity, S , of solutions of NaCl ¹⁷ at 15° (*in vacuo*, taking water at 4° as 10,000), with regard to the percentage amount, p , of the salt in solution shows that it is expressed with sufficient accuracy by the equation: $S_{15} = 9991.6 + 71.17p + 0.2140p^2$. For instance, for a solution of the composition $200\text{H}_2\text{O} + \text{NaCl}$, $p = 1.6$, and $S_{15} = 1.0106$. It is seen from the formula that the addition of water produces a contraction.¹⁸ The specific gravity ¹⁹ at certain temperatures and concentrations *in vacuo* referred to that of water at 4° as 10,000 ²⁰ is as follows:

	0°	15°	30°	100°
$p = 5$	10372	10353	10307	9922
10	10768	10728	10669	10278
15	11164	11107	11043	10652
20	11568	11501	11429	11043

It should be remarked that Baumé's hydrometer is graduated by taking a 10 per cent. solution of sodium chloride as 10° on the scale, and therefore gives approximately the percentage amount of the salt in

-17.6° according to De Coppet. Rüdorff states that for strong solutions the temperature of the formation of ice falls in proportion to the content of the compound, $\text{NaCl}, 2\text{H}_2\text{O}$ (per 100 grams of water) by 0.342° per 1 gram of salt, while De Coppet shows that there is no proportionality, in a strict sense, for either a percentage of NaCl or of $\text{NaCl}, 2\text{H}_2\text{O}$.

¹⁷ A collection of observations on the specific gravity of solutions of sodium chloride is given in my work cited in Chapter I., note 50.

¹⁸ If S_0 be the specific gravity of water, and S the specific gravity of a solution containing p per cent. of salt, then by mixing equal weights of water and the solution, we shall obtain a solution containing $\frac{1}{2}p$ of the salt, and if it be formed without contraction, then its specific gravity x will be determined by the equation: $\frac{2}{x} = \frac{1}{S_0} + \frac{1}{S}$, because the volume is equal to the weight divided by the density. In reality, the specific gravity is always found to be greater than that calculated on the supposition of an absence of contraction.

¹⁹ If the specific gravity is observed by weighing in air without making corrections for the expansion of the vessel, &c., a different result is naturally obtained. This must not be lost sight of in very exact researches.

²⁰ If the sp. gr. S_2 be found directly by dividing the weight of a solution by the weight of water at the same temperature and in the same volume, then the true sp. gr. S referred to water at 4° is found by multiplying S_2 by the sp. gr. of water at the temperature of observation.

a solution. Common salt is somewhat soluble in alcohol,²¹ but it is insoluble in ether or oils.

Common salt gives very few compounds²² or double salts; it is also decomposed with great difficulty and its dissociation is unknown.²³ But it is easily decomposed, both when fused and in solution, by the action of a galvanic current. If the dry salt is fused in a crucible and an electric current passed through it by immersing carbon or platinum electrodes in it (the positive electrode is made of carbon and the negative of platinum or mercury), it is **decomposed**, the suffocating gas, chlorine, being liberated at the positive pole and metallic sodium at the negative. Both of these act on water at the moment of their evolution; the sodium evolves hydrogen and forms caustic soda, and the chlorine may yield oxygen and form hydrochloric acid, so that on passing a current through a solution of common salt oxygen, chlorine, and hydrochloric acid will appear at the positive pole (anode), and hydrogen and caustic soda at the negative pole.^{23a} Thus salt, like other salts, is decomposed by the action of an electric current into its ions, a metal and a haloid (Chap. III.).

With respect to the double decompositions of sodium chloride it should be observed that they are most varied, and serve as the means for obtaining nearly all the other compounds of sodium and chlorine. **The double decompositions of sodium chloride** are almost exclusively based on the possibility of the metal sodium being exchanged for hydrogen and other metals. But neither hydrogen nor any other metal can directly displace the sodium from sodium chloride, and the replacement of the sodium in sodium chloride by hydrogen and various

²¹ According to Schiff, 100 grams of alcohol, containing p per cent. by weight of C_2H_5O , dissolves at 15° —

$p = 10$	20	40	60	80
28.5	22.6	13.2	5.9	1.2 gram NaCl

²² Amongst the double salts formed by sodium chloride, that obtained by Ditte (1870) by the evaporation of the solution remaining after heating sodium iodate with hydrochloric acid until chlorine ceases to be liberated, is a remarkable one. Its composition is $NaIO_3, NaCl, 14H_2O$. Rammelsberg obtained a similar (perhaps the same) salt in well-formed crystals by the direct interaction of the two salts.

²³ In the flame of a Bunsen's burner (see Chap. XIII.), $NaCl$ gives sodium, doubtless under the reducing action of the elements carbon and hydrogen. In the presence of an excess of hydrochloric acid in the flame (when the sodium would form sodium chloride), no sodium is formed in the flame and the salt does not communicate its usual coloration.

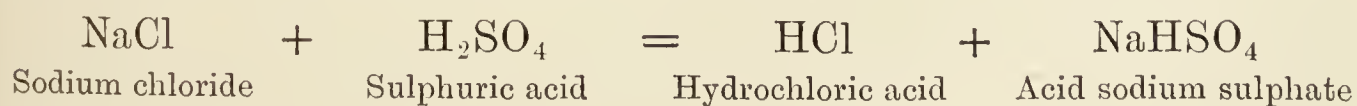
^{23a} There is no doubt, however, but that chloride of sodium is also decomposed in its aqueous solutions with the separation of sodium, and that it does not simply enter into double decomposition with the water ($NaCl + H_2O = NaHO + HCl$). This is seen from the fact that when a saturated solution of $NaCl$ is rapidly decomposed by an electric current, a large amount of chlorine appears at the anode and a sodium amalgam forms at the mercury cathode, which acts but slowly upon the strong solution of salt. Salt is now converted into chlorine and caustic soda on an industrial scale by this method.

metals can only take place by the transference of the sodium into some other combination. If hydrogen or a metal, M, be combined with an element X, then the double decomposition, $\text{NaCl} + \text{MX} = \text{NaX} + \text{MCl}$ takes place. Such double decompositions take place under special conditions, sometimes completely and sometimes only partially, as we shall endeavour to explain. In order to acquaint ourselves with the double decompositions of sodium chloride, we shall follow the methods employed in practice to procure compounds of sodium and of chlorine from common salt. For this purpose we shall first describe the treatment of sodium chloride with sulphuric acid for the preparation of hydrochloric acid and sodium sulphate. We shall then describe the substances obtained from hydrochloric acid and sodium sulphate. Chlorine itself, and nearly all the compounds of this element, may be procured from hydrochloric acid, whilst sodium carbonate, caustic soda, metallic sodium itself, and all its compounds may be obtained from sodium sulphate.

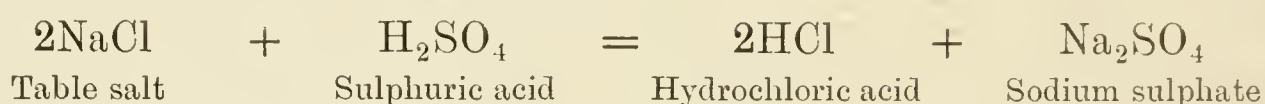
Even in the animal organism salt undergoes similar changes, furnishing the sodium, alkali, and hydrochloric acid which take part in the processes of animal life.

Its necessity as a constituent in the food both of human beings and of animals becomes evident when we consider that both hydrochloric acid and salts of sodium are found in the substances which are separated out from the blood into the stomach and intestines. Sodium salts are found in the blood and in the bile which is elaborated in the liver and acts on the food in the alimentary canal, whilst hydrochloric acid is found in the acid juices of the stomach (over 4 per cent.). Chlorides of the metals are always found in considerable quantities in the urine, and if they are excreted they must be replenished in the organism; and for the replenishment of the loss, substances containing chlorine compounds must be taken in food. Not only do animals consume those small amounts of sodium chloride which are found in drinking water or in plants or other animals, but many wild animals travel long distances in search of salt springs, and domestic animals which in their natural condition do not require salt, willingly take it, the functions of their organisms becoming much more regular from their doing so.

The action of sulphuric acid on sodium chloride.—If sulphuric acid is poured over common salt, even at the ordinary temperature, as Glauber observed, an odorous gas, hydrochloric acid, is evolved. The reaction which takes place consists in the sodium of the salt and the hydrogen of the sulphuric acid changing places:



At the ordinary temperature this reaction is not complete, but soon ceases (with the formation of the compound $\text{NaHSO}_4, \text{H}_2\text{SO}_4$). When the mixture is heated, the decomposition proceeds until, if there be sufficient salt present, all the sulphuric acid taken is converted into acid sodium sulphate. Any excess of acid will remain unaltered. If 2 molecules of sodium chloride (117 parts) be taken per molecule of sulphuric acid (98 parts), then on heating the mixture to a moderate temperature only one-half (58.5) of the salt will undergo change. Complete decomposition, after which no chlorine is left in the residue, proceeds *at a red heat only*. Then—



This double decomposition is the result of the action of the acid salt, NaHSO_4 , first formed, on sodium chloride, for the acid salt, since it contains hydrogen, itself acts like an acid, $\text{NaCl} + \text{NaHSO}_4 = \text{HCl} + \text{Na}_2\text{SO}_4$. By adding this equation to the first we obtain the second, which expresses the ultimate reaction. Hence in the above reaction, non-volatile or sparingly volatile table salt and sparingly volatile sulphuric acid are taken, and as the result of their reaction, after the hydrogen and sodium have exchanged places, there is obtained non-volatile sodium sulphate and gaseous hydrochloric acid. The fact of the latter being a gaseous substance forms the main reason for the reaction proceeding to the end. The HCl evolved is soluble in water, and its solution is usually called **hydrochloric** or **muriatic acid**. The mechanism of this kind of double decomposition, and the cause of the course of the reaction, are exactly the same as those we found in the decomposition of nitre (Chap. VI.) by the action of sulphuric acid. The sulphuric acid in each case displaces the other, volatile, acid.

Not only in these two instances, but in every instance, if a volatile acid can be formed by the substitution of the hydrogen of sulphuric acid for a metal, then this volatile acid will be formed. From this it may be concluded that the volatility of the acid should be considered as one of the causes of the progress of the reaction; and indeed if the acid be soluble but not volatile, or if the reaction take place in an enclosed space where the resulting acid cannot volatilise, or at the ordinary temperature when it does not pass into the state of elastic vapour—then the decomposition does not proceed to the end, but only up to a certain limit. In this respect the explanations given at the beginning of the nineteenth century by the French chemist Berthollet in his work ‘*Essai de Statique Chimique*,’ and elaborated and generalised

at the close of the nineteenth century, are very important. **The doctrine of Berthollet** starts from the supposition that the chemical reaction of substances is determined not only by the degrees of affinity between the different parts, but also by the relative masses of the reacting substances and by those physical conditions under which the reaction takes place. Two substances, containing the elements MX and NY, being brought into contact with each other, form by double decomposition the compounds MY and NX; but the formation of these two new compounds will not proceed to the end unless one of them is removed from the sphere of action. But it can only be removed if it possesses different physical properties from those of the other substances which are present with it. Either it must be a gas while the others are liquid or solid, or an insoluble solid while the others are liquid or soluble. The relative amounts of the resultant substances, if nothing separates out from their intermixture, depend only on the relative quantities of the substances MX and NY, and upon the degrees of attraction existing between the elements M, N, X, and Y; but however great their mass may be, and however considerable the attractions, still in any case, if nothing separates out from the sphere of action the decomposition will presently cease, **a state of equilibrium** will be established, and instead of two there will remain four substances in the mass: namely, a portion of the original bodies MX and NY, and a certain quantity of the newly formed substances MY and NX, it being assumed that neither MN nor XY nor any other substances are produced, as may for the present ²⁴ be admitted in the case of the double decomposition of salts in which M and N are metals and X and Y haloids. The sum total of existing data concerning the double decomposition of salts leads to the conclusion that from salts $MX + NY$ there always arises a certain quantity of NX and MY, as should be the case according to Berthollet's doctrine. In order that what is said in the following pages about the *modus operandi* of double saline decompositions may acquire its proper connection with other now prevalent chemical views, it is indispensable that some slight

²⁴ If MX and NY represent the molecules of two salts, and if there be *no third substance* present (such as water in a solution), the formation of XY would also be possible; for instance, chlorine and iodine are capable of combining together and with metals. Besides which the salts MX and NY or MY with NX may form double salts, and in general the matter may be complicated by the formation of other compounds besides MY and NX, and when a solvent participates in the action, and especially if present in large proportion, the phenomena must evidently become still more complex. Hence while placing before the reader a certain portion of the existing store of knowledge concerning the phenomena of double saline decompositions, I cannot consider the theory of the subject as complete, and have therefore limited myself to a few data, the completion of which must be sought in more detailed works on the subject of theoretical chemistry, without losing sight of what has been said above.

mention at least should be made of the reversibility of many reactions ^{24a} and of the phenomena of dissociation ^{24b}, as it is only in this way that the true unity of the principles acting in every chemical reaction stands forth. If a salt MX and a salt NY give salts MY + NX, and at the same time MY and NX are able to give MX + NY, it is evident that a state of equilibrium must somewhere ensue between the two opposite reactions, and be attained in equal degree from whichever side we start, if all the substances MX, NY, MY, and NX occur in one homogeneous medium such as a solution. In this lies the point of junction of Bergmann and Berthollet's different views. The first held that the measure of the affinities determines the ultimate reaction with the formation of MY + NX *in toto* if the affinities of the resultant bodies, i.e., of M to Y and N to X, be greater than the affinities in the original bodies, i.e., of M to X and N to Y, and that the reverse reaction is impossible—that is, that MY + NX cannot give any MX + NY, for the weaker cannot overcome the stronger. According to Berthollet, on the other hand, the only part played by affinity is that of distribution, the weaker affinities also playing their part in the general conflict. And although, from the essence of the matter, there are no means of directly measuring the force of affinity, yet logical sequence and the phenomena observed oblige us now to give preference to Berthollet's doctrine; and if there be no reaction between two given substances—for instance, oxygen and hydrogen—it does not indicate that there is no chemical affinity between the elements composing these substances, or that the affinity is too small to overcome the existing state of equilibrium, but only that there are not the necessary conditions for reaction; and that when these conditions are fulfilled a state of equilibrium and distribution will ensue, which will finish in one way or another according to the properties of the participating substances and the conditions in which they are placed. Thus oxygen and hydrogen react at high temperatures forming water, but the water then also

^{24a} The reversibility of many reactions, under certain conditions, is frequently expressed by the sign \rightleftharpoons (for instance $AB \rightleftharpoons A + B$ signifies that AB is able to split up into A and B, but that at the same time A is able, under the same conditions, to combine with B and give AB), which clearly shows that the thermo-chemical data of the evolution or absorption of heat are alone insufficient to determine the direction of a reaction, because if heat is evolved in one direction, it will be absorbed when the reaction proceeds in the opposite direction.

^{24b} As every double decomposition may be mentally reduced to a sum of decompositions and combinations, the fundamental principle of chemical mechanics is expressed in dissociation. In the sense in which it was enunciated by St. Claire-Deville, it throws light directly upon the influence of mass, the conditions of environment, of temperature, pressure, affinity and equilibrium, and hence the doctrine of Berthelot only acquired its true importance and meaning after the conception of dissociation had been established.

decomposes and dissociates to a certain degree. The matter evidently becomes far more complicated in this case, but all facts appear more complex when they become better known than they do at first sight.

It must be remembered that at the time when Berthollet, conjecturing much that was then unknown, understood the essence of chemical reactions in the case of salts, the modern conceptions of the atomic composition of bodies and of molecules were not known, but in expounding his theory we have made use of these fundamental conceptions in order to render the subject more easily understood.

And since, according to Berthollet's doctrine, when mMX of one salt comes into contact with nNY of another salt, there are formed certain quantities xMY and xNX , and there remains $m-x$ of the salt MX , and $n-x$ of the salt NY , if m be greater than n , then the maximum interchange could lead to $x=n$, whilst from the salts taken there would be formed $nMY + nNX + (m-n)MX$ —that is, a portion of one of the salts (MX) taken would remain unchanged because the reaction could only proceed (according to the conception of atoms) between nMX and nNY . If x were actually equal to n , the mass of the salt MX would not have any influence on the *modus operandi* of the reaction, which is equally in accordance with the teaching of Bergmann, who supposed double reactions to be independent of the mass and determined by affinity only. If M had more affinity for X than for Y , and N more affinity for Y than for X , then according to Bergmann there would be no decomposition whatever, and x would equal 0. If the affinity of M for Y and of N for X were greater than those in the original grouping, then the affinity of M for X and of N for Y would be overcome, and, according to Bergmann's doctrine, complete interchange would take place—i.e., x would equal n . According to Berthollet's teaching, if nothing be separated out and all the conditions (temperature, contact) for reaction be present, a distribution of M and N between X and Y will take place in every case, not only in proportion to the degrees of affinity, but also in proportion to the masses, so that with a small affinity and a large mass the same action can be produced as with a large affinity and a small mass. Therefore, (1) x will always be less than n and their ratio $\frac{x}{n}$ less than unity—that is, the decomposition will be expressed by the equation, $mMX + nNY = (m-x)MX + (n-x)NY + xMY + xNX$; (2) by increasing the mass m we increase the decomposition—that is, we increase x and the ratio $\frac{x}{(n-x)}$, until with an infinitely large quantity m the fraction $\frac{x}{n}$ will equal 1, and the

decomposition will be complete, however small the affinities uniting MY and NX may be ; and (3) by taking MX and NY or MY and NX we arrive at one and the same system *in either case*. These direct consequences of Berthollet's teaching are verified by experience. Thus, for example, a mixture of solutions of sodium nitrate and potassium chloride in all cases has exactly the same properties as a mixture of solutions of potassium nitrate and sodium chloride, of course on condition that the mixed solutions are of identical elementary composition, and have the same temperature, pressure, &c. But this identity of properties might either proceed from one system of salts passing entirely into the other (Bergmann's hypothesis) in conformity with the predominating affinities (for instance, from $\text{KCl} + \text{NaNO}_3$ there might arise $\text{KNO}_3 + \text{NaCl}$, if it be admitted that the affinities of the elements as combined in the latter system are greater than in the former) ; or, on the other hand, it might be because both systems by the interchange of a portion of their elements give one and the same state of equilibrium, as according to Berthollet's teaching. Experiment proves the latter hypothesis to be the true one. But before citing the historically most important experiments verifying Berthollet's doctrine, we must stop to consider the **conception of the mass** of the reacting substances. Berthollet understood by mass the actual relative quantity of a substance ; but now it is impossible to understand this term otherwise than as the number of molecules, for these act as chemical units, and in the special case of double saline decompositions it is better to take it as the number of equivalents. Thus in the reaction $\text{NaCl} + \text{H}_2\text{SO}_4$, the salt is taken in one equivalent and the acid in two. If $2\text{NaCl} + \text{H}_2\text{SO}_4$ react, then the numbers of equivalents of the two are equal, and so on. The **influence of mass** on the amount of decomposition $\frac{x}{n}$ forms the root of

Berthollet's doctrine, and we shall therefore first of all turn our attention to the establishment of this principle in relation to the double decomposition of salts.

About 1840 H. Rose²⁵ showed that water decomposes metallic sulphides like calcium sulphide, CaS , forming hydrogen sulphide, H_2S , notwithstanding the fact that the affinity of hydrogen sulphide, as an acid, for lime, CaH_2O_2 , as a base, causes them to react on each other, forming calcium sulphide and water, $\text{CaS} + 2\text{H}_2\text{O}$. Furthermore, Rose showed that the greater the amount of water acting on the calcium sulphide, the more complete is the decomposition. The results of this

²⁵ H. Rose is more especially known for having carefully studied and perfected several methods for the exact chemical analysis of many mineral substances. His predecessor in this branch of research was Berzelius, and his successor Fresenius.

reaction are evident from the fact that the hydrogen sulphide formed may be expelled from the solution by heating, and that the resulting lime is sparingly soluble in water. Rose clearly saw from this that such feeble agents, in a chemical sense, as carbonic anhydride and water, by acting in mass and for long periods of time in nature on the durable rocks, which resist the action of the most powerful acids, are able to bring about chemical change—to extract, for example, from rocks the bases, lime, soda, and potash. The influence of water in mass on antimonious chloride, bismuth nitrate, &c., is essentially of the same character. These substances give up to the water a quantity of acid which is greater in proportion as the mass of the water acting on them is greater.^{25a}

Barium sulphate, BaSO_4 , which is insoluble in water, when fused with sodium carbonate, Na_2CO_3 , gives, but not completely, barium carbonate, BaCO_3 (also insoluble), and sodium sulphate, Na_2SO_4 . If a solution of sodium carbonate acts on precipitated barium sulphate, the same decomposition is also effected (Dulong, Rose), but it is restricted by a limit and requires time. A mixture of sodium carbonate and sulphate is obtained in the solution and a mixture of barium carbonate and sulphate in the precipitate. If the solution be decanted off and a fresh solution of sodium carbonate be poured over the precipitate, then a fresh portion of the barium sulphate passes into barium carbonate, and so, by increasing the mass of the sodium carbonate, it is possible to entirely convert the barium sulphate into barium carbonate. If a definite quantity of sodium sulphate be added to the solution of sodium carbonate, then the latter will have no action whatever on the barium sulphate, because then a system in equilibrium, determined by the reverse action of the sodium sulphate on the barium carbonate and by the presence of both sodium carbonate and sulphate in the solution, is at once arrived at. On the other hand, if the mass of the sodium sulphate in the solution be great, then the barium carbonate is reconverted into sulphate until a definite state of equilibrium is attained between the two opposite reactions, producing barium carbonate by the action of the sodium carbonate and barium sulphate by the action of the sodium sulphate. The influence of mass is here evident.

^{25a} Historically the influence of the mass of water was the first well-observed phenomenon in support of Berthollet's teaching, and it should not now be forgotten. In double decompositions taking place in dilute solutions where the mass of water is large, its influence, notwithstanding the weakness of affinities, must be great, according to the very essence of Berthollet's doctrine.

As explaining the action of the mass of water, the experiments of Pattison Muir (1879) are very instructive. These experiments demonstrate that the decomposition of bismuth chloride is the more complete the greater the relative quantity of water, and the less the mass of the hydrochloric acid which forms one of the products of the reaction.

Another most important principle of Berthollet's teaching is the existence of **a limit of exchange decomposition, or the attainment of a state of equilibrium**. In this respect the determinations of Malaguti (1857) are historically the most important. He took a mixture of solutions of equivalent quantities of two salts, MX and NY, and judged the amount of the resulting exchange from the composition of the precipitate produced by the addition of alcohol. When, for example, zinc sulphate and sodium chloride (ZnSO_4 and 2NaCl) were taken, there were produced by exchange sodium sulphate and zinc chloride. A mixture of zinc sulphate and sodium sulphate was precipitated by an excess of alcohol, and it appeared from the composition of the precipitate that 72 per cent. of the salts taken had been decomposed. When, however, a mixture of solutions of sodium sulphate and zinc chloride was taken, the precipitate presented the same composition as before—that is, about 28 per cent. of the salts taken had been subjected to decomposition. In a similar experiment with a mixture of sodium chloride and magnesium sulphate, $2\text{NaCl} + \text{MgSO}_4$ or $\text{MgCl}_2 + \text{Na}_2\text{SO}_4$, about half of the metals underwent the decomposition, which may be expressed by the equation $4\text{NaCl} + 2\text{MgSO}_4 = 2\text{NaCl} + \text{MgSO}_4 + \text{Na}_2\text{SO}_4 + \text{MgCl}_2$. A no less clear limit expressed itself in another of Malaguti's researches in which he investigated the above-mentioned reversible reactions of the insoluble salts of barium. When, for example, barium carbonate and sodium sulphate ($\text{BaCO}_3 + \text{Na}_2\text{SO}_4$) were taken, about 72 per cent. of the salts were decomposed, that is, were converted into barium sulphate and sodium carbonate. But when the two latter salts were taken, about 19 per cent. of them passed into barium carbonate and sodium sulphate. Probably the end of the reaction was not reached in either case, because this would require a considerable time and a uniformity of conditions attainable with difficulty.

Gladstone (1855) took advantage of the colour of solutions of different ferric salts for determining the measure of exchange between metals, and this is better because then everything remains in solution. A solution of ferric thiocyanate has a most intense red colour, and by making a comparison between the colour of the resulting solutions and the colour of solutions of known strength it was possible to judge very closely the quantity of the thiocyanate formed. This colorimetric method of determination has an important significance as being the first in which a method was applied for determining the composition of a solution without the removal of any of its component parts. When Gladstone took equivalent quantities of ferric nitrate and potassium thiocyanate— $\text{Fe}(\text{NO}_3)_3 + 3\text{KCNS}$ —only 13 per cent. of the salts underwent decomposition. On increasing the mass of the latter salt the

quantity of ferric thiocyanate formed increased, but even when more than 300 equivalents of potassium thiocyanate were taken a portion of the iron still remained as nitrate. It is evident (according to Berthollet's theory) that the affinity acting between Fe and NO_3 and between K and CNS on the one hand is greater than the affinity acting between Fe and CNS, together with the affinity of K for NO_3 , on the other hand. The investigation of the variation of the fluorescence of quinine sulphate, as well as the variation of the rotation of the plane of polarisation of nicotine, gave in the hands of Gladstone many proofs of the entire applicability of Berthollet's doctrine, and in particular demonstrated the influence of mass which forms the chief distinctive feature of the doctrine of Berthollet, a doctrine but little appreciated in his own time. (Determinations showing the influence of the mass of the water are, however, wanting.)

At the beginning of the year 1860 the doctrine of the limit of reaction and of the influence of mass on the process of chemical transformations received very important support in the researches of Berthelot and Peau de Saint-Gilles on the formation of the ethereal salts RX from the alcohols ROH and acids HX, when water is also formed. This conversion is essentially very similar to the formation of salts, but differs in that it proceeds slowly at the ordinary temperature, extending over whole years, and is not complete, that is, it has a distinct limit determined by a reverse reaction; thus an ethereal salt RX with water gives an alcohol ROH and an acid HX—up to the limit generally corresponding with two-thirds of the alcohol taken, if the action proceed between molecular quantities of alcohol and acid. Thus ordinary alcohol, $\text{C}_2\text{H}_5\text{OH}$, with acetic acid, $\text{HC}_2\text{H}_3\text{O}_2$, gives rapidly when heated, or slowly at the ordinary temperature, the system $\text{ROH} + \text{HX} + 2\text{RX} + 2\text{H}_2\text{O}$, whether we start from $3\text{RHO} + 3\text{HX}$ or from $3\text{RX} + 3\text{H}_2\text{O}$. The process and completion of the reaction in this instance are very easily observed, because the quantity of free acid is easily determined from the amount of alkali requisite for its saturation, as neither the alcohol nor the ethereal salt acts on litmus or other reagents for detecting acids. Under the influence of an increased mass of alcohol the reaction proceeds further. If two molecules of alcohol, RHO, be taken for every one molecule of acetic acid, HX, then instead of 66 per cent., 83 per cent. of the acid passes into ethereal salt, and with fifty molecules of RHO nearly all the acid is etherised. The researches of N. A. Menschutkin touched in detail on many important aspects of the same subject, such as the influence of the composition of the alcohol and acid on the limit and rate of exchange—but these, as well as other details, must be looked for in special treatises on organic

and theoretical chemistry. In any case the study of etherification has supplied chemical mechanics with clear and valuable data, which directly confirm the two fundamental propositions of Berthollet; the influence of mass, and the limit of reaction—that is, the equilibrium between opposite reactions.²⁶

A very important epoch in the history of Berthollet's doctrine was attained when, in 1867, the Norwegian chemists, Guldberg and Waage, expressed it as an algebraical formula. They defined the active mass as the number of molecules contained in a given volume, and assumed, as follows from the spirit of Berthollet's teaching, that the action between the substances was equal to the *product* of the masses of the reacting substances. Hence if the salts MX and NY be taken in equivalent quantities ($m = 1$ and $n = 1$) and the salts MY and NX are not added to the mixture but proceed from it, and if k represent the coefficient of the rate of the action of MX on NY and k' the same coefficient for the pair MY and NX, then we shall have at the moment when the decomposition equals x a measure of action for the first pair: $k(1 - x)(1 - x)$, and for the second pair $k'xx$, and a state of equilibrium or limit will be reached when $k(1 - x)^2 = k'x^2$, whence the ratio $k/k' = [x/(1 - x)]^2$. Therefore in the case of the action of alcohol on an acid, when $x = \frac{2}{3}$, the magnitude $k/k' = 4$, that is, the reaction of the alcohol on the acid is four times as fast as that of the ethereal salt on water. If the ratio k/k' be known, then *the influence of mass may be easily determined* from it. Thus if instead of one molecule of alcohol two be taken, then the equation will be $k(2 - x)(1 - x) = k'xx$, whence $x = 0.85$ or 85 per cent., which agrees closely with the result of experiment. If 300 molecules of alcohol be taken, then x proves to be approximately 100 per cent., which is also found to be the case by experiment.^{26a}

But it is impossible to subject the formation of salts to any process directly analogous to that which is so conveniently effected in etherification. Many efforts have, however, been made to solve the problem of the measure of reaction in this case also. Thus, for example,

²⁶ With respect to double saline decompositions, it is also necessary to mention the researches of Wiedemann on the decomposing action of a mass of water on the ferric salts, which could be determined by measuring the magnetism of the solutions, because the ferric oxide (soluble colloid) set free by the water is less magnetic than the ferric salts.

^{26a} From the above it follows that an excess of acid should influence the reaction like an excess of alcohol. It is in fact shown by experiment that if two molecules of acetic acid be taken to one molecule of alcohol, 84 per cent. of alcohol is etherified. If with a large preponderance of acid or of alcohol certain discrepancies are observed, their cause must be looked for in the incomplete correspondence of the conditions and external influences.

Khichinsky (1866), Petrieff (1885), and many others investigated the distribution of metals and haloid groups in the case of one metal and several haloids, taken in excess, as acids ; or conversely with an excess of bases, the distribution of these bases with relation to an acid ; in cases where a portion of the substances forms a precipitate and a portion remains in solution. But such complex cases, although they in general confirm Berthollet's teaching (for instance, a solution of silver nitrate gives some silver oxide with lead oxide, and a solution of nitrate of lead precipitates some lead oxide under the action of silver oxide, as Petrieff demonstrated), still, owing to the complexity of the phenomena (for instance, the formation of basic and double salts), they cannot give simple results. But much more instructive and complete are researches like those made by Pattison Muir (1876), who took the simple case of the precipitation of calcium carbonate, CaCO_3 , from the mixture of solutions of calcium chloride and sodium or potassium carbonate, and found in this case that not only was the rate of action (for example, in the case of $\text{CaCl}_2 + \text{Na}_2\text{CO}_3$, 75 per cent. of CaCO_3 was precipitated in five minutes, 85 per cent. in thirty minutes, and 94 per cent. in two days) determined by the temperature, the relative masses, and the amount of water (a large mass of water decreases the rate), but that the limit of decomposition was also dependent on these influences. However, even in researches of this kind the conditions of reaction are complicated by the non-uniformity of the media, inasmuch as a portion of the substance is obtained or remains in the form of a precipitate, so that the system is heterogeneous. The investigation of double saline decompositions offers many difficulties which cannot be considered as yet entirely overcome. Although many efforts have long since been made, the majority of the researches were carried on in aqueous solutions, and as water is itself a saline compound and able to combine with salts and enter into double decomposition with them, such reactions taking place in solutions in reality present very complex cases.²⁷ In

²⁷ As an example two methods may be mentioned, Thomsen's and Ostwald's. Thomsen (1869) applied a thermo-chemical method to exceedingly dilute solutions without taking the water into further consideration. He took solutions of caustic soda containing $100\text{H}_2\text{O}$ per NaHO , and sulphuric acid containing $\frac{1}{2}\text{H}_2\text{SO}_4 + 100\text{H}_2\text{O}$. In order that these solutions may be mixed in such quantities that atomic proportions of acid and alkali would act, for forty grams of caustic soda (which answers to its equivalent) there should be employed 49 grams of sulphuric acid, and then +15,689 heat units would be evolved. If the normal sodium sulphate so formed be mixed with n equivalents of sulphuric acid, a certain amount of heat is absorbed, namely, a quantity equal to $\frac{n \cdot 1650}{n + 0.8}$ heat units. An equivalent of caustic soda, in combining with an equivalent of nitric acid, evolves +13,617 units of heat, and the augmentation of the amount of nitric acid entails an absorption of heat for each equivalent equal to -27 units ; so also in combining with hydrochloric acid +13,740 heat units are evolved, and for each equivalent of

this sense the reaction between alcohols and acids is much more simple, and therefore its significance in confirmation of Berthollet's doctrine is of particular importance. The only cases which can be compared with

hydrochloric acid beyond this amount there are absorbed -32 heat units. Thomsen mixed each one of three neutral salts, sodium sulphate, sodium chloride, and sodium nitrate, with an acid which is not contained in it; for instance, he mixed a solution of sodium sulphate with one of nitric acid and determined the number of heat units then absorbed. An absorption of heat ensued because a normal salt was taken in the first instance, and the mixture of all the above normal salts with acid produces an absorption of heat. The amount of heat absorbed enabled him to obtain an insight into the process taking place in this mixture, for sulphuric acid added to sodium sulphate absorbs a considerable quantity of heat, whilst hydrochloric and nitric acids absorb a very small amount of heat in this case. By mixing an equivalent of sodium sulphate with various numbers of equivalents of nitric acid, Thomsen observed that the amount of heat absorbed increased more and more as the amount of nitric acid was increased; thus when HNO_3 was taken per $\frac{1}{2}\text{Na}_2\text{SO}_4$, 1,752 heat units were absorbed per equivalent of soda contained in the sodium sulphate. When twice as much nitric acid was taken, 2,026 heat units, and when three times as much, 2,050 heat units were absorbed. Had the double decomposition been complete in the case where one equivalent of nitric acid was taken per equivalent of Na_2SO_4 , then according to calculation from similar data there should have been absorbed $-2,989$ units of heat, while in reality only $-1,752$ units were absorbed. Hence Thomsen concluded that a displacement of only about two-thirds of the sulphuric acid had taken place—that is, the ratio $k:k'$ for the reactions $\frac{1}{2}\text{Na}_2\text{SO}_4 + \text{HNO}_3$ and $\text{NaNO}_3 + \frac{1}{2}\text{H}_2\text{SO}_4$ is equal, as for ethereal salts, to 4. By taking this figure and admitting the above supposition, Thomsen found that for all mixtures of soda with nitric acid, and of sodium nitrate with sulphuric acid, the amounts of heat followed Guldberg and Waage's law; that is, the limit of decomposition reached was greater, the greater the mass of acid added. The relation of hydrochloric to sulphuric acid gave the same results. Therefore the researches of Thomsen fully confirm the hypotheses of Guldberg and Waage and the doctrine of Berthollet.

Whilst retaining essentially the methods of Thomsen, Ostwald (1876) determined the variation of the sp. gr. (and afterwards of volume), proceeding in the same dilute solutions, on the saturation of acids by bases, and in the decomposition of the salts of one acid by the other, and arrived at conclusions of just the same nature as Thomsen's. Ostwald's method will be clearly understood from an example. A solution of caustic soda containing an almost molecular (40 grams) weight per litre had a specific gravity of 1.04051. The specific gravities of solutions of equal volume and equivalent composition of sulphuric and nitric acids were 1.02970 and 1.03084 respectively. On mixing the solutions of NaHO and H_2SO_4 there was formed a solution of Na_2SO_4 of sp. gr. 1.02959; hence there ensued a decrease of specific gravity which we will term Q , equal to $1.04051 + 1.02970 - 2(1.02959) = 0.01103$. So also the specific gravity after mixture of the solutions of NaHO and HNO_3 was 1.02633, and therefore $Q = 0.01869$. When one volume of the solution of nitric acid was added to two volumes of the solution of sodium sulphate, a solution of sp. gr. 1.02781 was obtained, and therefore the resultant decrease of sp. gr.,

$$Q_1 = 2(1.02959) + 1.03084 - 3(1.02781) = 0.00659.$$

Had there been no chemical reaction between the salts, then, according to Ostwald's reasoning, the specific gravity of the solutions would not have changed, and if the nitric acid had entirely displaced the sulphuric acid Q_2 would be $= 0.01869 - 0.01103 = 0.00766$. It is evident that a portion of the sulphuric acid was displaced by the nitric acid. But the measure of displacement is not equal to the ratio between Q_1 and Q_2 , because a decrease of sp. gr. also occurs on mixing the solution of sodium sulphate with sulphuric acid, whilst the mixing of the solutions of sodium nitrate and nitric acid only produces a slight variation of sp. gr. which falls within the limits of experimental error. Ostwald

these reactions for simplicity are those double decompositions, investigated by G. G. Gustavson, which take place between CCl_4 and RBr_n on the one hand, and CBr_4 and RCl_n on the other. This case is convenient for investigation inasmuch as the RCl_n and RBr_n taken (such as BCl_3 , SiCl_4 , TiCl_4 , POCl_3 , and SnCl_4) belong to those substances which are decomposed by water, whilst CCl_4 and CBr_4 are not decomposed by water; and therefore, by heating, for instance, a mixture of CCl_4 + SiBr_4 it is possible to arrive at a conclusion as to the amount of interchange by treating the product with water, which decomposes the SiBr_4 left unchanged and the SiCl_4 formed by the exchange, and therefore by determining the composition of the product acted on by the water it is possible to form a conclusion as to the amount of decomposition. The mixture was always formed with equivalent quantities—for instance, $4\text{BCl}_3 + 3\text{CBr}_4$. It appeared that there was no exchange whatever on simple intermixture, but that it proceeded slowly, when the mixture was heated (for example, with the mixture above mentioned, at 123° 4.86 per cent. of Cl was replaced by Br after 14 days' heating, and 6.83 per cent. after 28 days, and 10.12 per cent. when heated at

deduces from similar data the same conclusions as Thomsen, and thus reconfirms the formula deduced by Guldberg and Waage, and the teaching of Berthollet.

The participation of water is seen still more clearly in the methods adopted by Ostwald than in those of Thomsen, because in the saturation of solutions of acids by alkalies (which Kremers, Reinhold, and others had previously studied) there is observed, not a contraction, as might have been expected from the quantity of heat which is then evolved, but an expansion, of volume (a decrease of specific gravity, if we calculate as Ostwald did in his first investigations). Thus by mixing 1,880 grams of a solution of sulphuric acid of the composition $\text{SO}_3 + 100\text{H}_2\text{O}$, occupying a volume of 1,815 c.c., with a corresponding quantity of a solution $2(\text{NaHO} + 5\text{H}_2\text{O})$, whose volume is 1,793 c.c., we obtain not 3,608 but 3,633 c.c., an expansion of 25 c.c. per gram molecule of the resulting salt, Na_2SO_4 . It is the same in other cases. Nitric and hydrochloric acids give a still greater expansion than sulphuric acid, and potassium hydroxide than sodium hydroxide, whilst a solution of ammonia gives a contraction. The relation to water must be considered as the cause of these phenomena. When sodium hydroxide and sulphuric acid dissolve in water they develop heat and give a vigorous contraction. After mutual saturation they form the salt Na_2SO_4 , which retains the water but feebly and evolves but little heat with it, i.e., in other words, has little affinity for water. In the saturation of sulphuric acid by soda the water is, as it were, displaced from a stable combination and passes into an unstable combination; hence an expansion (decrease of sp. gr.) takes place. It is not the reaction of the acid on the alkali, but the reaction of water, that produces the phenomenon by which Ostwald desires to measure the degree of salt formation. The volume of $\text{H}_2\text{SO}_4 = 53.3$, that of $2\text{NaHO} = 37.4$; there is produced $2\text{H}_2\text{O}$, volume = 36, + Na_2SO_4 , volume = 53.6. There react 90.7 c.c., and on saturation there result 89.6 c.c.; consequently contraction again ensues. Hence the phenomena studied by Ostwald depend but little on the measure of the reaction of the salts, and more on the relations of the dissolved substances to water. It may be concluded, therefore, on the basis of what has been said, that on taking water into consideration the phenomena studied by Thomsen and Ostwald are much more complex than they at first appear, and that this method can scarcely lead to a correct interpretation as to the distribution of acids between bases.

150° for 60 days). A limit was always reached which corresponded with that of the reverse system, that is, in the given instance, of the system $4\text{BBr}_3 + 3\text{CCl}_4$. In this last 89.97 per cent. of bromine in the BBr_3 was replaced by chlorine; that is, there were obtained 89.97 molecules of BCl_3 and there remained 10.02 molecules of BBr_3 , and therefore the same state of equilibrium was reached as that given by the system $4\text{BCl}_3 + 3\text{CBr}_4$. Both systems gave one and the same state of equilibrium at the limit, which is in agreement with the essence of Berthollet's doctrine.²⁸

Thus we now find ample confirmation from various quarters for the

²⁸ G. G. Gustavson's researches, which were conducted in the laboratory of the St. Petersburg University in 1871-72, are among the first in which the measure of the affinity of the elements for the halogens is recognised with perfect clearness in the limit of substitution and in the rate of reaction. The researches conducted by Prof. A. L. Potilitzin (of which mention will be made in Chap. XI., note 66), in the same laboratory, touch on another aspect of the same problem which has not yet made much progress, notwithstanding its importance and the fact that the theoretical side of the subject (thanks especially to Guldberg and van't Hoff) has since been rapidly pushed forward. If the researches of Gustavson took account of the influence of mass, and were more fully supplied with data concerning velocities and temperatures, they would be very important, because of the great significance which the case considered has for the understanding of double saline decompositions 'in the absence of water.'

Furthermore, Gustavson showed that the greater the atomic weight of the element (B, Si, Ti, As, Sn) combined *with chlorine* the greater the amount of chlorine replaced by bromine by the action of CBr_4 , and consequently the less the amount of bromine replaced by chlorine by the action of CCl_4 on bromine compounds. For instance, for chlorine compounds the percentage of substitution (at the limit) is—

BCl_3	SiCl_4	TiCl_4	AsCl_3	SnCl_4
10.1	12.5	43.6	71.8	77.5

It should be observed, however, that Thorpe, on the basis of his experiments, denies the universality of this conclusion. I may mention one conclusion which it appears to me may be drawn from the above-cited figures of Gustavson, if they are subsequently verified even within narrow limits. If CBr_4 be heated with RCl_4 , then an exchange of the bromine for chlorine takes place. But what would be the result if it were mixed with CCl_4 ? Judging by the magnitude of the atomic weights, $\text{B} = 11$, $\text{C} = 12$, $\text{Si} = 28$, about 11 per cent. of the chlorine would be replaced by bromine. But to what does this point? I think that it shows the existence of a motion of the atoms in the molecule. The mixture of CCl_4 and CBr_4 does not remain in a condition of static equilibrium; not only are the molecules contained in it in a state of motion, but so also are the atoms in the molecules, and the above figures show the measure of their translation under these conditions. The bromine in the CBr_4 is, *within the limit*, substituted by the chlorine of the CCl_4 in a quantity of about 11 out of 100: that is, some of the atoms of bromine previously to this moment in combination with one atom of carbon pass over to the other atom of carbon, and the chlorine passes over from this second atom of carbon to replace it. Therefore, also, in the homogeneous mass CCl_4 all the atoms of Cl do not remain constantly combined with the same atoms of carbon, and *there is an exchange of atoms between different molecules in a homogeneous medium also*. This hypothesis may in my opinion explain certain phenomena of dissociation, but though mentioning it I do not consider it worth while to dwell upon it. I will only observe that a similar hypothesis of dynamic or mobile equilibrium may be brought into agreement with the doctrine of a store of internal chemical energy.

following rules of Berthollet, applying them to double saline decompositions in a uniform (homogeneous) medium. 1. From two salts MX and NY containing different haloids and metals there result from their reaction two others, MY and NX, but such a substitution will not proceed to the end unless one product passes from the sphere of action. 2. This reaction is limited by the existence of an equilibrium between MX, NY, MY, and NX, because a reverse reaction ($MY + NX = MX + NY$) is quite as possible as the direct reaction $MX + NY = MY + NX$. 3. This limit is determined both by the measure of the active affinities and by the relative masses of the substances as measured most simply by the relative number of the reacting molecules. 4. Other conditions being constant, the chemical action is proportional to the product of the chemical masses in action.²⁹

Thus if the salts MX and NY after reaction partly form salts MY and NX, a state of equilibrium is reached and the reaction ceases; but if one of the resultant compounds, in virtue of its physical properties, passes from the sphere of action of the remaining substances, then the reaction will continue, because the relation between the masses is altered. This exit from the sphere of action depends on the physical properties of the substance and on the conditions under which the reaction takes place. Thus, for instance, the salt NX may, in the case of reaction between solutions, separate as a precipitate—an insoluble substance—while the other three substances remain in solution, or it may pass into vapour, and in this manner also pass away from the sphere of action of the remaining substances. Let us now suppose that it passes away in some form or other from the sphere of action of the remaining substances—for instance, that it is transformed into a precipitate or vapour—then a fresh reaction and a re-formation of the salt NX will set in, and so on. In consequence of the physical properties of the resultant substances, the reaction is then able to proceed to completion notwithstanding the possible weakness of the attraction existing between the elements entering into the composition of the resultant substance NX. Naturally, if it is formed of elements having a considerable degree of affinity, the complete position is considerably facilitated.

Such a representation of the *modus operandi* of chemical

²⁹ Berthollet's doctrine is hardly at all affected in principle by showing that there are cases in which there is no decomposition between salts, because the affinity may be so small that even a large mass would still give no observable displacements. The fundamental condition for the application of Berthollet's doctrine, as well as Deville's doctrine of dissociation, lies in the reversibility of reactions. Just as there are practically non-volatile and non-decomposable bodies, so also we must admit the existence of practically irreversible reactions (for instance, $CCl_4 + 2H_2O = CO_2 + 4HCl$).

transformations is applicable with great clearness to a number of reactions studied in chemistry, and, what is especially important, the application of this aspect of Berthollet's teaching does not in any way require the determination of the measure of affinity acting between the substances present. For instance, the action of ammonia on solutions of salts; the displacement, by its means, of basic hydrates insoluble in water; the separation of volatile nitric acid by the aid of non-volatile sulphuric acid, as well as the decomposition of common salt by means of sulphuric acid, when gaseous hydrochloric acid is formed—may be taken as examples of reactions which proceed to the end, inasmuch as one of the resultant substances is entirely removed from the sphere of action, but they in no way indicate the measure of affinity.

Returning to the displacement of hydrochloric acid from common salt by sulphuric acid as further illustrating Berthollet's doctrine,³⁰ the fact may be cited that common salt may be entirely decomposed by nitric acid, with the formation of NaNO_3 and HCl , and conversely nitre may be completely decomposed by hydrochloric acid, just as they are decomposed by sulphuric acid. This only takes place, however, when, in the first instance, a large excess of nitric acid is taken, and in the second instance, an excess of hydrochloric acid, and when the resultant acid passes off. If sodium chloride is put into a porcelain evaporating basin, nitric acid added to it, and the mixture heated, a certain amount of both hydrochloric and nitric acids are expelled by the heat. Thus the nitric acid partially acts on the

³⁰ If a solution of common salt be mixed with a solution of magnesium sulphate, double decomposition may result in the formation of sodium sulphate and magnesium chloride, substances which are soluble in water; nothing is disengaged, and therefore the decomposition $2\text{NaCl} + \text{MgSO}_4 = \text{MgCl}_2 + \text{Na}_2\text{SO}_4$ cannot proceed to the end. However the sodium sulphate formed in this manner may be separated by freezing strong solutions. Complete separation of the sodium sulphate will naturally not take place, owing to a portion of the salt remaining in the solution, but Na_2SO_4 separates out in crystals. This kind of decomposition is made use of for the preparation of sodium sulphate from the residues left after the evaporation of sea-water, which contain a mixture of magnesium sulphate and common salt. A solution of copper sulphate is of a blue colour, while a solution of copper chloride is green. If we mix the two salts together the green tint is distinctly visible, so that by this means the presence of the copper chloride in the solution of copper sulphate is clearly seen. If now we add a solution of common salt to a solution of copper sulphate, a green coloration is obtained, which indicates the formation of copper chloride. In this instance it is not separated, but it is immediately formed on the addition of common salt, as it should be according to Berthollet's doctrine.

The complete formation of a metallic chloride from common salt can only occur, judging from the above, when it separates from the sphere of action. The salts of silver are instances in point, because silver chloride is insoluble in water; and therefore if we add a solution of sodium chloride to a solution of a silver salt, a precipitate of silver chloride and a solution of the sodium salt of that acid which was in the silver salt are formed.

sodium chloride, but on heating, as both acids are volatile, they are both converted into vapour; and therefore the residue will contain a mixture of certain quantities of NaCl and NaNO_3 . If a fresh quantity of nitric acid be then added, reaction will again set in, a certain portion of hydrochloric acid is again evolved, and on heating is expelled together with nitric acid. If this be repeated several times, it is possible to expel all the hydrochloric acid, and to obtain only sodium nitrate in the residue. If, on the contrary, sodium nitrate is treated with hydrochloric acid and heated, a portion of the nitric acid is displaced, and on heating, the excess of hydrochloric acid passes away together with the nitric acid formed. On repeating this process, it is possible to displace the nitric acid by an excess of hydrochloric acid, just as it was possible to displace the hydrochloric acid by an excess of nitric acid. The influence of the mass of the substance in action and the influence of volatility are here very distinctly seen. As in these instances HCl is displaced by HNO_3 , and conversely, it may be affirmed that sulphuric acid does not displace hydrochloric acid because of an especially high degree of affinity, but that this reaction only takes place because the sulphuric acid is not volatile, whilst the hydrochloric acid which is formed is volatile.

The preparation of hydrochloric acid in the laboratory and on a large scale is based upon these data. In the first instance an excess of sulphuric acid is employed³¹ in order that the reaction may proceed easily at a low temperature, whilst on a large scale, when it is necessary to economise every material, equivalent quantities are taken in order to obtain the normal salt Na_2SO_4 and not the acid salt, which would require twice as much acid.

In chemical works the decomposition of sodium chloride by means of sulphuric acid is carried out on a very large scale, chiefly with a view

³¹ The apparatus shown in fig. 52 (Chap. VI., note 12) is generally employed for the preparation of small quantities of hydrochloric acid. Common salt is placed in the retort; the salt is generally previously fused, as it otherwise froths and boils over in the apparatus. When the apparatus is arranged, sulphuric acid mixed with water is poured down the thistle funnel into the retort. Strong sulphuric acid (about half as much again as the weight of the salt) is usually taken, and is diluted with a small quantity of water (half) if it is desired to retard the action, as in using strong sulphuric acid the action immediately begins with great vigour. The mixture, at first without the aid of heat and then at a moderate temperature (in a water-bath), evolves hydrochloric acid. Commercial hydrochloric acid contains many impurities; it is usually purified by distillation, the middle portions being collected. It is purified from arsenic by adding FeCl_3 , distilling, and rejecting the first third of the distillate. If free hydrochloric acid gas is required, it is passed through a vessel containing strong sulphuric acid to dry it, and is collected over a mercury bath.

Phosphoric anhydride absorbs hydrogen chloride (Bailey and Fowler, 1888; $2\text{P}_2\text{O}_5 + 3\text{HCl} = \text{POCl}_3 + 3\text{HPO}_3$) at the ordinary temperature, so that the gas cannot be dried by this substance.

to the preparation of normal sodium sulphate, the hydrochloric acid being a by-product.^{31a} The furnace employed is termed a **salt-cake furnace**. It is represented in fig. 74, and consists of the following two parts: the pan B and the roaster C—an enclosed space built up of large bricks *a* and enveloped on all sides by the smoke and flames from the fire grate, F. The ultimate decomposition of the salt by the sulphuric acid is accomplished in the roaster. But the first decomposition of sodium chloride by sulphuric acid does not require so high a temperature as the ultimate decomposition, and is therefore carried on in the front and cooler portion, B, the bottom of which is heated by gas flues. When the reaction in this portion ceases and the evolution of hydro-

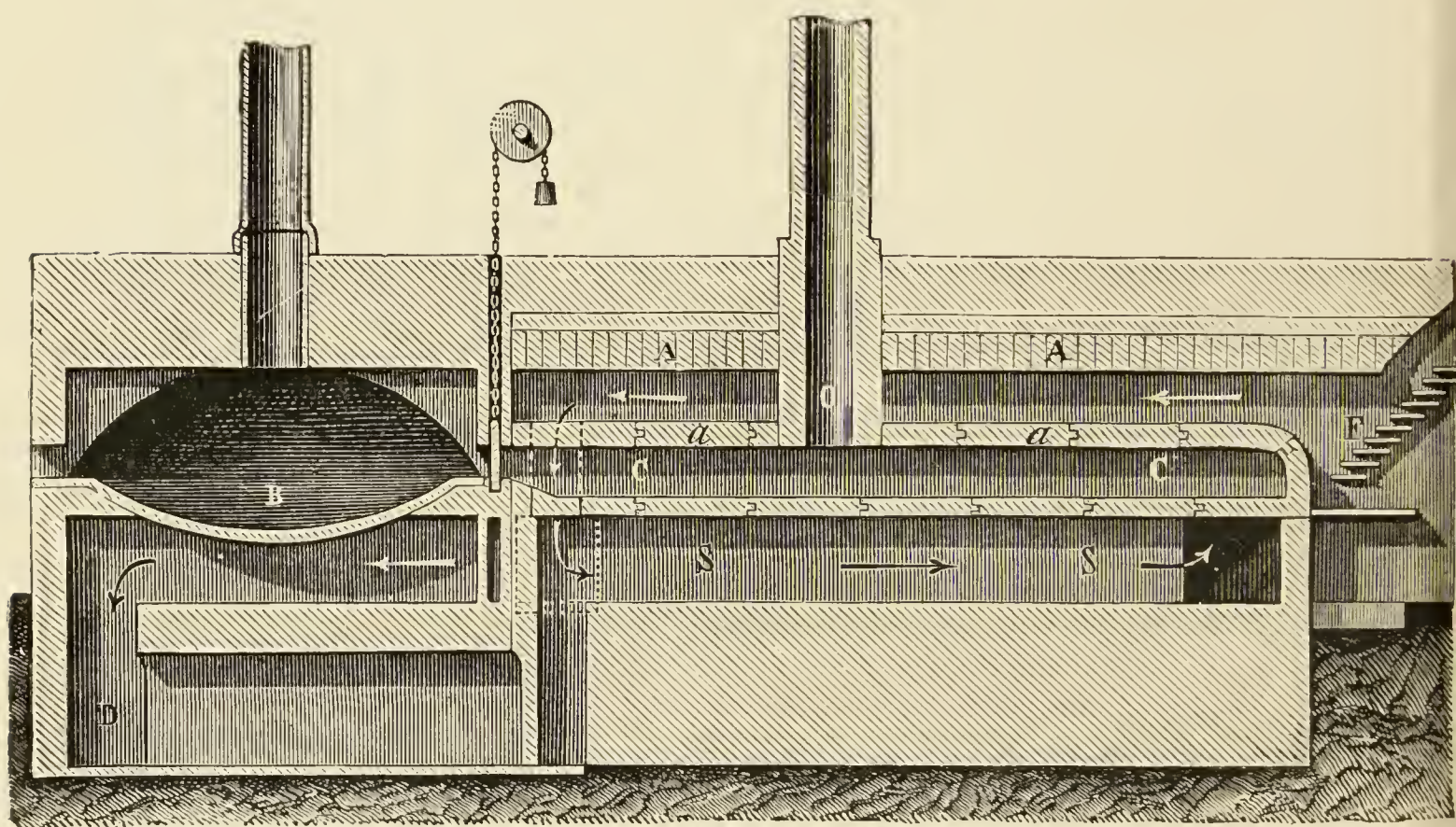


FIG. 74.—Section of a salt-cake furnace. B, pan in which the sodium chloride and sulphuric acid are first mixed and heated. C, muffle for the ultimate decomposition.

chloric acid stops, the mass of acid sodium sulphate is removed from B and thrown into the roaster C, where the reaction is completed. Normal sodium sulphate, which we shall afterwards describe, remains in the roaster. For the present we will only turn our attention to the hydrochloric acid evolved in B and C.

The hydrochloric acid gas evolved is subjected to condensation by dissolving it in water.³² If the apparatus in which the decomposition

^{31a} In chemical works where sulphuric acid of 60° Baumé (22 per cent. of water) is employed, 117 parts of sodium chloride are taken to about 125 parts of sulphuric acid.

³² As, in works which treat common salt in order to obtain sodium sulphate, the hydrochloric acid is sometimes held to be of no value (has no sale), it might be allowed

is accomplished were hermetically closed, and only presented one outlet, the escape of the hydrochloric acid would only proceed through the escape pipe intended for this purpose. But as it is impossible to construct a perfectly hermetically closed furnace it is necessary to increase

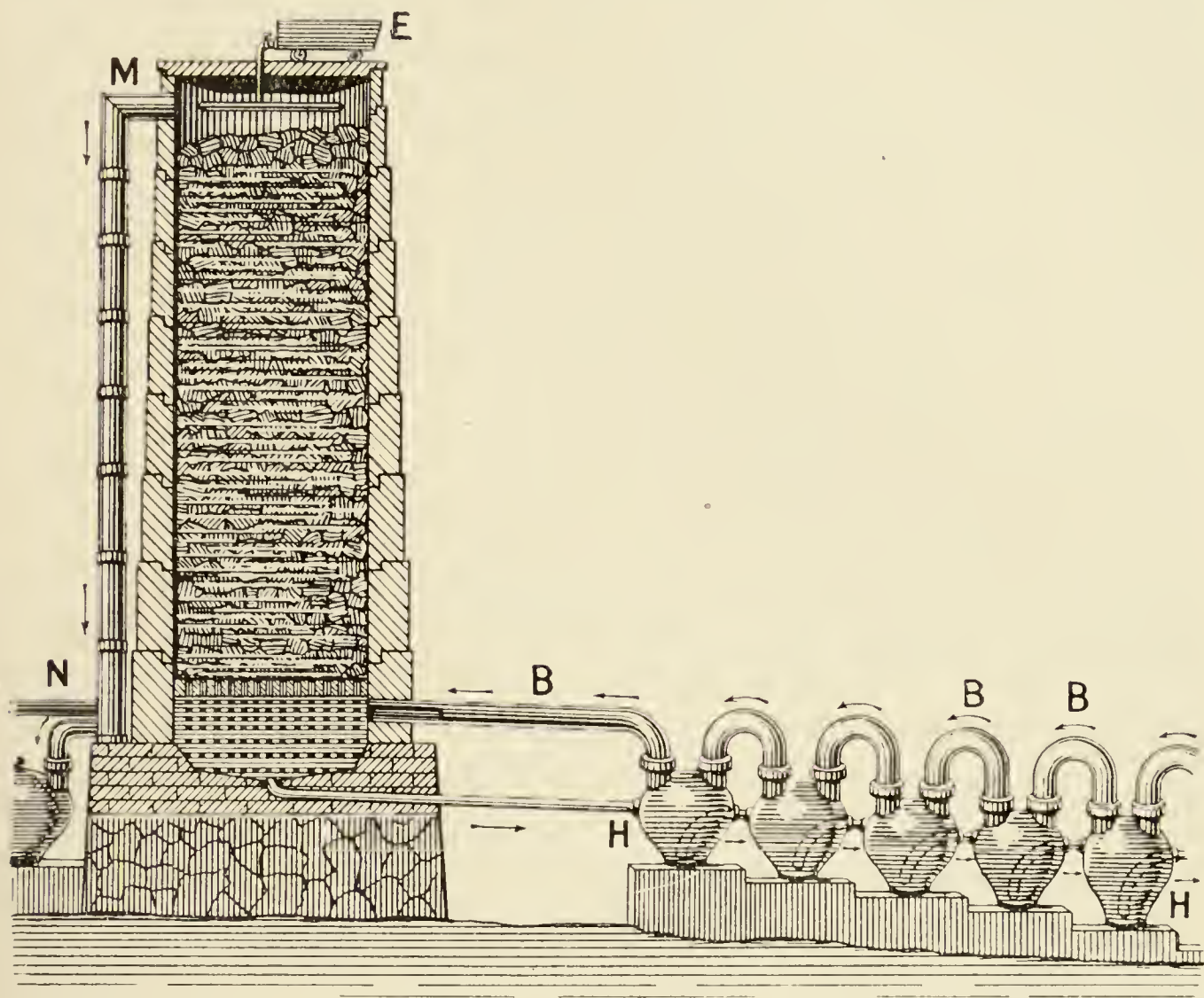


FIG. 75.—Apparatus used in works for the condensation of hydrogen chloride, evolved in furnaces. The gas is drawn through the tubes B, B, . . . up the coke tower, down the tube M N and into the furnace shaft, while the water passes from E, down the coke tower, and then through the vessels H, H, . . ., dissolving the hydrogen chloride.

the draught by artificial means, or to compel the hydrochloric acid gas to pass through those arrangements in which it is to be condensed.

to escape with the waste furnace gases into the atmosphere, which would greatly injure the air of the neighbourhood and destroy all vegetation. In all countries, therefore, there are laws forbidding the manufacture from being carried on in this manner, and requiring the absorption of the hydrochloric acid by water at the works themselves, and not permitting the solution to be run into rivers and streams, in which it would spoil the water. It may be remarked that the absorption of hydrochloric acid presents no particular difficulties (the absorption of sulphurous acid is much more difficult) because hydrochloric acid has a great affinity for water and gives a hydrate which boils at above 100° . Hence, even steam and hot water, as well as weaker solutions, can be used for absorbing the acid. However, Warder (1888) showed that weak solutions of composition $\text{H}_2\text{O} + n\text{HCl}$ when boiled (the residue will be almost $\text{HCl}, 8\text{H}_2\text{O}$) evolve (not water but) a solution containing $\text{H}_2\text{O} + 445n\text{HCl}$; for example, on distilling $\text{HCl}, 10\text{H}_2\text{O}$, a distillate of the composition $\text{HCl}, 23\text{H}_2\text{O}$ is first obtained. As the strength of the residue becomes greater, so also does that of the distillate, and therefore in order to completely absorb hydrochloric acid it is necessary in the end to have recourse to water.

This is done by connecting the ends of the tubes through which the hydrochloric acid gas escapes from the furnace with high chimneys, where a strong draught is set up by the combustion of the fuel. This causes a current of hydrochloric acid gas to pass through the absorbing apparatus in a definite direction. Here it encounters a current of water flowing in the opposite direction, by which it is absorbed. It is not customary to cause the acid to pass through the water, but only to bring it into contact with the surface of the water (to avoid increasing the resistance). The absorption apparatus consists of large earthenware vessels having four orifices, two above and two lateral ones in the wide central portion of each vessel. The upper orifices serve for connecting the vessels together by tubes, and the hydrochloric acid gas escaping from the furnace passes through these tubes. The water for absorbing the acid enters at the upper, and flows out from the lower, vessel, passing through the lateral orifices in the vessels. The water flows from the chimney towards the furnace, and it is therefore evident that the out-flowing water will be the most nearly saturated with acid, of which it actually contains about 20 per cent. The absorption in these vessels is not complete. The ultimate absorption of the hydrochloric acid is carried on in so-called **coke towers**, which usually consist of two adjacent chimneys. A lattice-work of bricks is laid on the bottom of these towers, in which coke is piled up to the top. Water, distributing itself over the coke, trickles down to the bottom of the tower, and in so doing absorbs the hydrochloric acid gas passing upwards.

It will be readily understood that hydrochloric acid may be obtained from all other metallic chlorides.³³ It is frequently formed in other reactions, many of which we shall meet with in the further course of this work. It is, for instance, formed by the direct action of water on sulphur chloride, phosphorus chloride, antimony chloride, &c.

Hydrochloric acid, HCl , is a colourless gas having a pungent, suffocating odour and an acid taste. This gas fumes in air and attracts moisture, because it forms vapour containing a compound of

³³ Those metallic chlorides which are decomposed to a greater or less degree by water correspond with feeble bases. Such are, for example, MgCl_2 , AlCl_3 , SbCl_3 , BiCl_3 . The decomposition of magnesium chloride (and also carnallite) by sulphuric acid proceeds at the ordinary temperature; water decomposes MgCl_2 to the extent of 50 per cent. when aided by heat, and *may be employed as a convenient method for the production of hydrochloric acid*. Hydrochloric acid is also produced by the ignition in a stream of hydrogen of certain metallic chlorides, especially of those metals which are easily reduced—for instance, silver chloride. Lead chloride, when heated to redness in a current of steam, gives hydrochloric acid and lead oxide. The frequency of the formation of hydrochloric acid is understood from the fact that it is a substance which is comparatively very stable, resembling water in this respect, and most probably even more stable than water, because, at a high temperature and even under the action of light, chlorine decomposes water, with the formation of hydrochloric acid.

hydrochloric acid and water. Hydrochloric acid is liquefied by cold, and, under a pressure of 40 atmospheres, into a colourless liquid of sp. gr. about 1.26,³⁴ boiling-point about -84° , freezing-point about -110° , and absolute boiling-point $+50^{\circ}$. We have already seen (Chap. I.) that hydrochloric acid combines very energetically **with water**, and in so doing evolves a considerable amount of heat. The solution saturated in the cold attains a density 1.23. On heating such a solution—containing about 45 per cent. of acid—the hydrochloric acid gas is expelled with only a slight admixture of aqueous vapour. But it is impossible to separate the whole of the hydrochloric acid from the water by this means, as could be done in the case of an ammoniacal solution. The temperature required for the evolution of the gas rises and reaches 110° – 111° , and after this remains constant—that is, a solution having a constant boiling-point is obtained (as with HNO_3), which, however, does not (Roscoe and Dittmar) present a constant composition under different pressures, because the hydrate is decomposed in distillation, as is seen from the determinations of its vapour density (Bineau). Judging from the facts (1) that with decrease of the pressure under which the distillation proceeds the solution of constant boiling-point approaches to a composition of 25 per cent. of hydrochloric acid,³⁵ (2) that by passing a stream of dry air through a solution of hydrochloric acid there is obtained in the residue a solution which also approaches to 25 per cent. of acid, and the more nearly as the temperature falls,³⁶ (3) that many of the properties of solutions of hydrochloric acid vary distinctly according as they contain more or less than 25 per cent. of hydrochloric acid (for instance, antimonious sulphide gives hydrogen sulphide with a stronger acid, but is not acted on by a weaker solution), also a stronger solution fumes in the air, &c., and (4) that the composition $\text{HCl}, 6\text{H}_2\text{O}$ corresponds with 25.26 per cent. HCl —judging from all these data, and also from the loss of pressure which occurs in the combination of hydrochloric acid with water, it may be said that they form a **definite hydrate** of the composition $\text{HCl}, 6\text{H}_2\text{O}$. Besides this not clearly defined hydrate there exists also a crystallo-hydrate, $\text{HCl}, 2\text{H}_2\text{O}$,³⁷ which is formed by the

³⁴ According to Ansdell (1880) the sp. gr. of liquid hydrochloric acid at 0° is 0.908; at 11.67° , 0.854; at 22.7° , 0.808; and at 33° , 0.748. Hence it is seen that the expansion of this liquid is greater than that of gases (Chap. II., note 34).

³⁵ According to Roscoe and Dittmar, at a pressure of three atmospheres the solution of constant boiling-point contains 18 per cent. of hydrogen chloride, and at a pressure of one-tenth of an atmosphere, 23 per cent. The percentages are intermediate at pressures between these two.

³⁶ At 0° , 25 per cent., at 100° , 20.7 per cent.; Roscoe and Dittmar.

³⁷ This crystallo-hydrate (obtained by Pierre and Puchot, and investigated by Roozeboom) is analogous to $\text{NaCl}, 2\text{H}_2\text{O}$. The crystals $\text{HCl}, 2\text{H}_2\text{O}$ at -22° have a specific

absorption of hydrochloric acid by the fuming acid at a temperature of -23° . It crystallises and melts at -18° .³⁸

gravity 1.46; the vapour pressure (under dissociation) of the solution having a composition $\text{HCl}, 2\text{H}_2\text{O}$ at -24° is 760, at -19° , 1,010, at -18° , 1,057, and at -17° , 1,112 mm. of mercury. In a solid state the crystallo-hydrate at -17.7° has the same pressure, whilst at lower temperatures it is much less: at -24° about 150, at -19° about 580 mm. A mixture of fuming hydrochloric acid with snow reduces the temperature to -38° . If another equivalent of water is added to the hydrate $\text{HCl}, 2\text{H}_2\text{O}$ at -18° , the temperature of solidification falls to -25° , and the hydrate $\text{HCl}, 3\text{H}_2\text{O}$ is formed (Pickering, 1893).

³⁸ According to Roscoe, at 0° one *hundred* grams of water at a pressure p (in millimetres of mercury) dissolve—

$p =$	100	200	300	500	700	1,000
Grams HCl	65.7	70.7	73.8	78.2	81.7	85.6

At a pressure of 760 millimetres and temperature t , one *hundred* grams of water dissolve—

$t =$	0	8°	16°	24°	40°	60°
Grams HCl	82.5	78.3	74.2	70.0	63.3	56.1

Bakhius Roozeboom (1886) showed that at t° solutions containing c grams of hydrogen chloride per 100 grams of water may (with the variation of the pressure p) be formed together with the crystallo-hydrate $\text{HCl}, 2\text{H}_2\text{O}$;

$t =$	-23.8°	-21°	-19°	-18°	-17.7°
$c =$	84.2	86.8	92.6	98.4	101.4
$p =$	—	334	580	900	1,073 mm.

The last combination answers to the melted crystallo-hydrate $\text{HCl}, 2\text{H}_2\text{O}$, which splits up at temperatures above -17.7° . At a constant atmospheric pressure when there are no crystals—

$t =$	-24°	-21°	-18°	-10°	0°
$c =$	101.2	98.3	95.7	89.8	84.2

From these data it is seen that the hydrate $\text{HCl}, 2\text{H}_2\text{O}$ can exist in a liquid state, which is not the case with the hydrates of carbonic and sulphurous anhydrides, chlorine, &c.

According to Marignac, the specific heat c of a solution $\text{HCl} + m\text{H}_2\text{O}$ (at about 30° , taking the specific heat of water as 1) is given by the expression—

$$c(36.5 + m18) = 18m - 28.39 + 140/m - 268/m^2,$$

if m be not less than 6.25. For example, for $\text{HCl} + 25\text{H}_2\text{O}$, $c = 0.877$.

According to Thomsen's data, the amount of heat Q , expressed in thousands of calories, evolved in the solution of 36.5 grams of gaseous hydrochloric acid in $m\text{H}_2\text{O}$ or $18m$ grams of water is equal to—

$m =$	2	4	10	50	400
$Q =$	11.4	14.3	16.2	17.1	17.3

In these quantities is included the latent heat of liquefaction, which must be taken as from 5 to 9 thousand calories per molecular quantity of hydrogen chloride.

The researches of Scheffer (1888) on the rate of diffusion (in water) of solutions of hydrochloric acid show that the coefficient of diffusion k decreases with the amount of water n , if the composition of the solution is $\text{HCl}, n\text{H}_2\text{O}$ at 0° :

$n =$	5	6.9	9.8	14	27.1	129.5
$k =$	2.31	2.08	1.86	1.67	1.52	1.39

It also appears that strong solutions diffuse more rapidly into dilute solutions than into water.

The specific gravities S at 15° , taking water at its maximum density (4°) as 10,000, for solutions containing p per cent. of hydrogen chloride are—

p	S	p	S
5	10,242	25	11,266 ³⁹
10	10,490	30	11,522
15	10,744	35	11,773
20	11,001	40	11,997

Solutions of hydrochloric acid present all the **properties of an energetic acid**. They not only transform blue vegetable colouring matter into red, and disengage carbonic acid gas from carbonates, &c., but they also completely saturate bases, even such energetic ones as potash, lime, &c. In a dry state, however, hydrochloric acid does not alter vegetable dyes, and does not effect many double decompositions which take place easily in the presence of water.⁴⁰ This is explained by the fact that the gaseous elastic state of the hydrochloric acid prevents its entering into reaction. However, incandescent iron, zinc, sodium, &c., act on gaseous hydrochloric acid, displacing the hydrogen and leaving half a volume of hydrogen for each volume of hydrochloric acid gas; this reaction may serve for determining the composition of hydrochloric

³⁹ The formula $S = 9,991.6 + 49.43p + 0.0571p^2$, up to $p = 25.26$, which answers to the hydrate $\text{HCl}, 6\text{H}_2\text{O}$ mentioned above, gives the specific gravity. Above this percentage $S = 9,785.1 + 65.10p - 0.240p^2$. The rise of specific gravity with an increase of percentage (or the differential $\frac{ds}{dp}$) reaches a maximum at about 25 per cent. The intermediate solution, $\text{HCl}, 6\text{H}_2\text{O}$, is further distinguished by the fact that the variation of the specific gravity with variation of temperature is a constant quantity, so that the specific gravity of this solution is equal to 11,352.7 ($1 - 0.000447t$), where 0.000447 is the coefficient of expansion of the solution. In the case of more dilute solutions, as with water, the specific gravity per 1° (or the differential $\frac{ds}{dt}$) rises with the temperature.

$p = 0$	5	10	15	20
$S_0 - S_{15} = 7.2$	23	38	52	64
$S_{15} - S_{30} = 34.1$	42	50	59	67

Whilst for solutions which contain a greater proportion of hydrogen chloride than $\text{HCl}, 6\text{H}_2\text{O}$, these coefficients *decrease* with a rise of temperature; for instance, for 30 per cent. of hydrogen chloride, $S_0 - S_{15} = 88$ and $S_{15} - S_{30} = 87$ (according to Marignac's data). In the case of $\text{HCl}, 6\text{H}_2\text{O}$ these differences are constant, and equal 76.

Thus the formation of two definite hydrates, $\text{HCl}, 2\text{H}_2\text{O}$ and $\text{HCl}, 6\text{H}_2\text{O}$, of hydrochloric acid may be accepted upon the basis of many facts. But both of them, if they occur in a liquid state, dissociate with great facility into hydrogen chloride and water, and are completely decomposed when distilled.

⁴⁰ Even a solution of perfectly dry HCl (dried by phosphoric anhydride) in dry benzene does not act upon dry carbonates (Kahlenberg, 1902), naturally because these salts are insoluble in benzene. But dry HCl acts upon dry oleate of copper, because this is soluble in benzene (Chap. I., note 49).

acid. Combined with water, hydrochloric acid acts as an acid much resembling nitric acid⁴¹ in its energy and in many of its reactions; however, the latter contains oxygen, which is disengaged with great ease, and so very frequently acts as an oxidiser, which hydrochloric acid is not capable of doing. The majority of metals (even those which do not displace the H from H_2SO_4 , but which, like copper, decompose it to the limit of SO_2) displace the hydrogen from hydrochloric acid. Thus hydrogen is disengaged by the action of zinc, and even of copper and tin.⁴² Only a few metals withstand its action: for example, gold and platinum. Lead in compact masses is only feebly acted upon, because the lead chloride formed is insoluble and prevents the further action of the acid on the metal. The same is to be remarked with respect to the feeble action of hydrochloric acid on mercury and silver, because the compounds of these metals, AgCl and HgCl , are insoluble in water. **Metallic chlorides** are not only formed by the action of hydrochloric acid on the metals, but also by many other methods; for instance, by the action of hydrochloric acid on the carbonates, oxides, and hydroxides, and also by the action of chlorine on metals and certain of their compounds. Metallic chlorides have a composition MCl (for example, NaCl , KCl , AgCl , HgCl) if the metal replaces hydrogen, equivalent for equivalent, or, as it is said, if it is monatomic or univalent. In the case of bivalent metals, they have a composition MCl_2 ; for example, CaCl_2 , CuCl_2 , PbCl_2 , HgCl_2 , FeCl_2 , MnCl_2 . The composition of the haloid salts of other metals determines their atomicity; for example, AlCl_3 , PtCl_4 , &c. Many metals, for instance, Fe, give several degrees of combination with chlorine (FeCl_2 , FeCl_3), as with hydrogen. In their composition the metallic chlorides differ from the corresponding oxides, in that the O is replaced by Cl_2 , as should follow from the law of substitution, because oxygen gives OH_2 , and is consequently di-atomic, whilst chlorine forms HCl , and is therefore univalent. So, for instance, ferrous oxide, FeO , corresponds with ferrous chloride, FeCl_2 , and the oxide Fe_2O_3 with ferric chloride, Fe_2Cl_6 or FeCl_3 , as is also seen from the origin of these compounds, for FeCl_2 is obtained by the action of hydrochloric acid on ferrous oxide or carbonate and FeCl_3 by its action on ferric oxide. In a word, all the typical properties of acids are shown by hydrochloric acid.

⁴¹ Thus, for instance, with feeble bases they evolve in dilute solutions (Chap. III., note 53) almost equal amounts of heat; their relation to sulphuric acid is quite identical. They both form fuming solutions as well as hydrates; they both form solutions of constant boiling-point.

⁴² Ribalkin (1891) found that copper begins to disengage hydrogen at 100° , and that chloride of copper begins to give up its chlorine to hydrogen gas at 230° ; for silver these temperatures are 117° and 200° —that is, there is less difference between them.

and all the typical properties of salts by the metallic chlorides derived from it. Acids and salts without any oxygen bear the name of **haloid salts**; for instance, HCl is a haloid acid, NaCl a haloid salt, chlorine a halogen. The capacity of hydrochloric acid to give, by its action on bases, MO, a metallic chloride, MCl_2 , and water, is limited at high temperatures by the reverse reaction, $MCl_2 + H_2O = MO + 2HCl$, and the more pronounced the basic properties of MO the feebler is the reverse action, while for feeble bases such as Al_2O_3 , MgO, &c., this reverse reaction proceeds with ease. Metallic chlorides corresponding with the peroxides either do not exist, or are easily decomposed with the disengagement of chlorine. Thus there is no compound $BaCl_4$ corresponding with the peroxide BaO_2 . Metallic chlorides having the general aspect of salts, like their representative sodium chloride, are, as a rule, easily fusible, more so than the oxides (for instance, CaO is fusible at a furnace heat, whilst $CaCl_2$ is easily fused) and many other salts. Under the action of heat many chlorides are more stable than the oxides, and some can even be converted into vapour; thus corrosive sublimate, $HgCl_2$, is particularly volatile, whilst the oxide HgO decomposes at a red heat. Silver chloride, AgCl, is fusible and is decomposed with difficulty, whilst Ag_2O is easily decomposed. The majority of the metallic chlorides are soluble in water, but silver chloride, cuprous chloride, mercurous chloride, and lead chloride are sparingly soluble in water, and are therefore easily obtained as precipitates when solutions of the salts of these metals are mixed with a solution of any chloride or even with hydrochloric acid. The metal contained in a haloid salt may often be replaced by another metal, or even by hydrogen, just as is the case with a metal in an oxide. Thus, copper displaces mercury from a solution of mercuric chloride, $HgCl_2 + Cu = CuCl_2 + Hg$, and hydrogen at a red heat displaces silver from silver chloride, $2AgCl + H_2 = Ag_2 + 2HCl$. These, and a whole series of similar reactions, form the typical methods of double saline decompositions. The measure of decomposition and the conditions under which reactions of double saline decomposition proceed in one or the other direction are determined by the properties of the compounds which take part in the reaction, and of those capable of formation at the particular temperature, &c., employed, as was shown in the preceding portions of this chapter, and as will be frequently found hereafter.

If hydrochloric acid enters into double decomposition with basic oxides and their hydrates, this is only due to its acid properties; and for the same reason it rarely enters into double decomposition with acids and acid anhydrides. Sometimes, however, it combines with the

latter, as, for instance, with the anhydride of sulphuric acid, forming the compound SO_3HCl ; and in other cases it acts on acids, giving up its hydrogen to their oxygen and forming chlorine, as will be seen in the following chapter.

Hydrochloric acid, as may already be concluded from the composition of its molecule, belongs to the monobasic acids, and does not, therefore, give true acid salts (like HNaSO_4 or HNaCO_3); nevertheless many metallic chlorides, formed from powerful bases, are capable of **combining with hydrochloric acid**, just as they combine with water, or with ammonia, or give double salts. Compounds have long been known of hydrochloric acid with auric, platinic, and antimonious chlorides, and other similar metallic chlorides corresponding with very feeble bases. But Berthelot, Engel, and others have shown that the capacity of HCl for combining with M_nCl_n is much more frequently encountered than was previously supposed. Thus, for instance, dry hydrochloric acid when passed into a solution of zinc chloride (containing an excess of the salt) gives in the cold (0°) a compound, $\text{HCl}, \text{ZnCl}_2, 2\text{H}_2\text{O}$, and at the ordinary temperature, $\text{HCl}, 2\text{ZnCl}_2, 2\text{H}_2\text{O}$, just as it is able at low temperatures to form the crystallo-hydrate, $\text{ZnCl}_2, 2\text{H}_2\text{O}$ (Engel, 1886). Similar compounds are obtained with $\text{CdCl}_2, \text{CuCl}_2, \text{HgCl}_2, \text{Fe}_2\text{Cl}_6$, &c. (Berthelot, Ditte, Cheltzoff, Lachinoff, and others). These compounds with hydrochloric acid are generally more soluble in water than the metallic chlorides themselves, so that whilst hydrochloric acid decreases the solubility of M_nCl_n , corresponding with energetic bases (for instance, sodium or barium chlorides), it increases the solubility of the metallic chlorides corresponding with feeble bases (cadmium chloride, ferric chloride, &c.). Silver chloride, which is insoluble in water, is soluble in hydrochloric acid. Hydrochloric acid also combines with certain unsaturated hydrocarbons (for instance, with turpentine, $\text{C}_{10}\text{H}_{16}, 2\text{HCl}$) and their derivatives.⁴³ **Sal-ammoniac**, or **ammonia hydrochloride**, $\text{NH}_4\text{Cl} = \text{NH}_3, \text{HCl}$, also belongs to this class of compounds. If hydrogen chloride gas is mixed with ammonia gas a solid compound consisting of equal volumes of each is immediately formed. The same

⁴³ When an unsaturated hydrocarbon, or, in general, an unsaturated compound, assimilates to itself the molecules $\text{Cl}_2, \text{HCl}, \text{SO}_3, \text{H}_2\text{SO}_4$, &c., the cause of the reaction is best conceived as the attainment of the limit. As nitrogen, besides the type NX_3 to which NH_3 belongs, gives compounds of the type NX_5 —for example, $\text{NO}_2(\text{OH})$ —the formation of the salts of ammonium should be understood in this way. NH_3 gives NH_4Cl because NX_3 is capable of giving NX_5 . But as saturated limiting compounds—for instance, $\text{SO}_3, \text{H}_2\text{O}, \text{NaCl}$, &c.—are also capable of combination even between themselves, it is impossible to deny the capacity of HCl also for combination. SO_3 combines with H_2O and also with HCl and the unsaturated hydrocarbons. It is impossible to recognise the distinction between atomic and molecular compounds, and to regard, for instance, PCl_3 as an atomic compound and PCl_5 as a molecular one.

compound is obtained on mixing solutions of the two gases. It is also produced by the action of hydrochloric acid on ammonium carbonate. Sal-ammoniac is usually prepared, in practice, by the last method.⁴⁴ The specific gravity of sal-ammoniac is 1.55. We have already seen (Chap. VI.) that sal-ammoniac, like all other ammonium salts, easily decomposes; for instance, by distillation with alkalies, and even partially when its solution is boiled. The other properties and reactions of sal-ammoniac, especially in solution, fully recall those already mentioned in speaking of sodium chloride. Thus, for instance, with silver nitrate it gives a precipitate of silver chloride; with sulphuric acid it gives hydrochloric acid and ammonium sulphate, and it forms double salts with certain metallic chlorides and other salts.⁴⁵ The aqueous solutions of the chlorides and of HCl are electrolytes, and give chlorine at the anode.

⁴⁴ Sal-ammoniac is prepared from ammonium carbonate, obtained in the dry distillation of nitrogenous substances (Chapter VI.), by saturating the resultant solution with hydrochloric acid. A solution of sal-ammoniac is thus produced, which is evaporated, and in the residue a mass is obtained containing also a mixture of various other, especially tarry, products of dry distillation. The sal-ammoniac is generally purified by sublimation. For this purpose iron vessels covered with hemispherical metallic covers are employed, or else simply clay crucibles covered by other crucibles. The upper portion, or head, of the apparatus of this kind will have a lower temperature than the lower portion, which is under the direct action of the flame. The sal-ammoniac volatilises when heated, and settles on the cooler portion of the apparatus. It is thus freed from many impurities, and is obtained as a crystalline crust, generally several centimetres thick, in which form it is commonly sold. The solubility of sal-ammoniac rises rapidly with the temperature: at 0°, 100 parts of water dissolve about 28 parts of NH_4Cl , at 50° about 50 parts, and at the ordinary temperature about 35 parts. This is sometimes taken advantage of for separating NH_4Cl from solutions of other salts.

⁴⁵ The solubility of sal-ammoniac in 100 parts of water (according to Alluard) is—

0°	10°	20°	30°	40°	60°	80°	100°	110°
28.40	32.48	37.28	41.72	46	55	64	73	77

A saturated solution boils at 115.8°. The specific gravity at 15°/4° of solutions of sal-ammoniac (water at 4° = 10,000) is given by $9,991.6 + 31.26p - 0.085p^2$, where p is the amount by weight of ammonium chloride in 100 parts by weight of solution. With the majority of salts the differential ds/dp increases, but here it decreases, with increase of p . For (unlike the sodium and potassium salts) a solution of the alkali *plus* a solution of acid occupy a greater volume than that of the resultant ammonium salt. In the solution of *solid* ammonium chloride a contraction, and not an expansion, generally takes place. It may further be remarked that solutions of sal-ammoniac have an acid reaction even when prepared from the salt remaining after prolonged washing of the sublimed salt with water (A. Stecherbakoff).

CHAPTER XI

THE HALOGENS: CHLORINE, BROMINE, IODINE, AND FLUORINE

ALTHOUGH hydrochloric acid, like water, is one of the most stable substances, it is nevertheless decomposed not only by the action of a galvanic current, but also by a high temperature.¹ Sainte-Claire Deville showed that decomposition occurs even at 1300°, because a cold tube (as with CO, Chap. IX.) covered with an amalgam of silver absorbs chlorine from hydrochloric acid in a red-hot tube, and the escaping gas contains hydrogen. V. Meyer and Langer (1885) demonstrated the decomposition of hydrochloric acid when mixed with nitrogen at 1690° in a platinum vessel, not only from the fact that the hydrogen diffuses through the platinum, but also from chlorine being obtained which liberated iodine from potassium iodide.² The usual method for

¹ The decomposition of fused sodium chloride by an electric current is employed as a means for the preparation of chlorine and sodium. A strong solution of hydrochloric acid is decomposed into equal volumes of chlorine and hydrogen by the action of an electric current. If sodium chloride and lead are melted in a crucible, the former being connected with the cathode and a carbon anode immersed in the lead, the lead dissolves the sodium, and chlorine is disengaged as gas. This electrolytic method is practised on a large scale.

At the close of the nineteenth century the evolution of chlorine at the anode in the electrolysis of solutions of the chlorides became of practical importance, especially in Germany, the United States, and England, the metals deposited at the cathode being, however, the chief object in the treatment. The chlorine here appears as a by- (and therefore cheap) product, and finds a market, mostly in the form of bleaching salts. For instance in the separation (and refining) of copper and zinc, these metals are obtained in the form of chlorides (by means of HCl or NaCl) in solution, and the electrolysis of this solution gives the metal and at the anode chlorine. In the electrolytic decomposition of carnallite for the preparation of magnesium: $\text{KMgCl}_3 = \text{KCl} + \text{Mg} + \text{Cl}_2$, &c. Strong solutions of NaCl by electrolysis, also give chlorine, and the sodium separated at the cathode (which is made of mercury to dissolve the sodium) gives caustic soda under the action of water, so that the chlorine here again appears as a by-product. Electrolytic methods will now undoubtedly replace all the above-described methods for the preparation of chlorine (from HCl, by removing the H by oxygen or higher oxides), especially where it is possible to employ water power instead of steam as a motive power for the dynamo.

² To obtain so high a temperature (at which the best kinds of porcelain soften) Langer and Meyer employed the dense graphitoidal carbon from gas retorts, and a powerful blast.

the preparation of chlorine consists in the abstraction of the hydrogen by oxidising agents.^{2a}

The hydrogen has to be abstracted from the hydrochloric acid. This is accomplished by nearly all oxidising substances, and especially by those which are able to evolve oxygen at a red heat (besides bases, such as mercury and silver oxides, which are able to give salts with hydrogen chloride), for example, manganese dioxide, potassium chlorate, chromic acid, &c. The decomposition essentially consists in the oxygen of the oxidising substance displacing the chlorine from 2HCl , forming water, H_2O , and setting the chlorine free, $2\text{HCl} + \text{O}$ (disengaged by the oxidising substances) $= \text{H}_2\text{O} + \text{Cl}_2$. Even nitric acid partially produces a like reaction; but its action is more complicated, and is accompanied by the formation of oxides of nitrogen, and it is therefore not suitable for the preparation of pure chlorine.³ But other oxidising substances which do not give volatile products with hydrochloric acid may be employed for the preparation of chlorine. Among these may be mentioned: potassium chlorate, acid potassium chromate, sodium manganate, manganese dioxide, &c. Since Scheele's time (1774) manganese dioxide has been commonly employed in the laboratory, and on a large scale, for the preparation of chlorine. The chemical process in this case may be represented as follows: an exchange takes place between 4HCl and MnO_2 , in which the manganese takes the place of the four atoms of hydrogen, or the chlorine and oxygen exchange

^{2a} The acid properties of hydrochloric acid were known when Lavoisier pointed out the formation of acids by the combination of water with the oxides of the non-metals, and there was therefore reason for thinking that hydrochloric acid was also an oxygen acid. When Scheele obtained chlorine by the action of hydrochloric acid on manganese peroxide he considered it as the acid contained in common salt. When it became known that chlorine gives hydrochloric acid with hydrogen, Lavoisier and Berthollet supposed it to be a compound with oxygen of an anhydride contained in hydrochloric acid. They supposed that hydrochloric acid contained water and the oxide of a particular radicle, and that chlorine was a higher degree of oxidation of this radicle *urias* (from the Latin name of hydrochloric acid, *acidum muriaticum*). It was only in 1811 that Gay-Lussac and Thénard in France, and Davy in England, arrived at the conclusion that the substance obtained by Scheele does not contain oxygen, nor give water with hydrogen under any conditions, and that there is no water in hydrochloric acid gas, and that chlorine is an elementary substance. They named it 'chlorine' from the Greek word *χλωρός*, signifying a green colour, because of the peculiar colour by which this gas is characterised.

³ However, nitric acid has been proposed as a means for obtaining chlorine, but by methods which have the drawback of being very complicated. As nitric acid is able to take up the hydrogen from HCl , chlorine is sometimes prepared by heating a mixture of nitric and hydrochloric acids. The resultant mixture of chlorine and lower oxides of nitrogen is subjected to the action of air and steam, which give HNO_3 again, and the chlorine remains as a gas together with nitrogen, in which form it is quite suitable for bleaching or for the preparation of bleaching powder, &c.

places—that is, MnCl_4 and $2\text{H}_2\text{O}$ are produced. The chlorine compound, MnCl_4 , obtained is very unstable; it splits up into chlorine, which as a gas passes from the sphere of action, and a salt, MnCl_2 , containing less chlorine, $\text{MnCl}_4 = \text{MnCl}_2 + \text{Cl}_2$.^{3a} The action of hydrochloric acid requires a temperature of about 100° . In the laboratory the **preparation of chlorine** is carried on in flasks, heated over a water-bath, by acting on manganese peroxide with hydrochloric acid or a

^{3a} This representation of the process of the reaction is the most natural. However, this decomposition is generally represented as if chlorine gave only one degree of combination with manganese, MnCl_2 , and therefore directly reacts in the following manner— $\text{MnO}_2 + 4\text{HCl} = \text{MnCl}_2 + 2\text{H}_2\text{O} + \text{Cl}_2$, in which case it is supposed that manganese peroxide, MnO_2 , breaks up, as it were, into manganous oxide, MnO , and oxygen, both of which react with hydrochloric acid, the manganous oxide acting upon HCl as a base, giving MnCl_2 and at the same time, $2\text{HCl} + \text{O} = \text{H}_2\text{O} + \text{Cl}_2$. In reality, a mixture of oxygen and hydrochloric acid does give chlorine at a red heat, and this reaction may also take place at the moment of its evolution in this case.

All the oxides of manganese (Mn_2O_3 , MnO_2 , MnO_3 , Mn_2O_7), with the exception of manganous oxide, MnO , disengage chlorine from hydrochloric acid, because manganous chloride, MnCl_2 , is the only compound of chlorine and manganese which exists as a stable compound, all the higher chlorides of manganese being unstable and evolving chlorine. MnCl_4 is unknown, but MnCl_3 has been obtained, but it readily (even in double salts) evolves chlorine. In general many of the higher compounds of chlorine with the metals are able to part with a portion of their chlorine. Amongst them may be mentioned antimony pentachloride, SbCl_5 , which splits up into chlorine and antimony trichloride when heated. **Cupric chloride**, corresponding with copper oxide, and having a composition CuCl_2 , similar to CuO , when heated parts with half its chlorine, just as barium peroxide evolves half its oxygen. This method may even be taken advantage of for the preparation of chlorine and cuprous chloride, CuCl . The latter attracts oxygen from the atmosphere, and in so doing is converted from a colourless substance into a green compound whose composition is $\text{Cu}_2\text{Cl}_2\text{O}$. With hydrochloric acid this substance gives cupric chloride ($\text{Cu}_2\text{Cl}_2\text{O} + 2\text{HCl} = \text{H}_2\text{O} + 2\text{CuCl}_2$), which has only to be dried and heated in order again to obtain chlorine. On this property is founded Deacon's process for the preparation of chlorine from hydrochloric acid with the aid of air and copper salts, by passing a mixture of air and hydrochloric acid at about 440° over bricks saturated with a solution of a copper salt (a mixture of solutions of CuSO_4 and Na_2SO_4). CuCl_2 is then formed by the double decomposition of the salt of copper and the hydrochloric acid; the CuCl_2 liberates chlorine and the CuCl forms $\text{Cu}_2\text{Cl}_2\text{O}$ with the oxygen of the air, which again gives CuCl_2 with 2HCl , and so on. However, all the HCl cannot be converted into chlorine by this process, but only about one half of it.

Magnesium chloride, which is obtained from sea-water, carnallite, &c., may serve not only as a means for the preparation of hydrochloric acid, but also of chlorine, because its basic salt (Mg_2OCl_2) when heated in the air gives magnesium oxide and chlorine (Weldon-Pechiney's process, 1884). Chlorine is now prepared on a large scale by this method. Besides these, Solvay and Mond's methods of preparing chlorine must be mentioned. The first is based upon the reaction, $\text{CaCl}_2 + \text{SiO}_2 + \text{O}(\text{air}) = \text{CaOSiO}_2 + \text{Cl}_2$, and the second on the action of the oxygen of the air (heated) upon MgCl_2 (and certain similar chlorides) $\text{MgCl}_2 + \text{O} = \text{MgO} + \text{Cl}_2$. The remaining MgO is treated with sal-ammoniac to re-form MgCl_2 ($\text{MgO} + 2\text{NH}_4\text{Cl} = \text{MgCl}_2 + \text{H}_2\text{O} + 2\text{NH}_3$) and the resultant NH_3 again converted into sal-ammoniac, so that hydrochloric acid is the only substance consumed. The latter processes have not found much application, having been ousted by electrolysis.

mixture of common salt and sulphuric acid ⁴ and washing the gas with water to remove hydrochloric acid.⁵ Chlorine cannot be collected over mercury, because it combines with it as with many other metals, and it is soluble in water; however, it is but slightly soluble in hot water or brine. Owing to its great weight (its density referred to hydrogen is about 36 and to air about 2.5) chlorine may be directly collected in a dry vessel by carrying the gas-conducting tube down to the bottom of the vessel. The chlorine will lie in a heavy layer at the bottom of the vessel, displace the air, and the extent to which it fills the vessel may be followed by its colour.⁶

⁴ The following proportions are accordingly taken by weight: 5 parts of powdered manganese peroxide, 11 parts of salt (best fused, to prevent its frothing), and 14 parts of sulphuric acid previously mixed with an equal volume of water. The mixture is heated in a salt bath, so as to obtain a temperature above 100°. The corks in the apparatus must be soaked in paraffin (otherwise they are corroded by the chlorine), and black india-rubber tubing smeared with vaseline must be used, not vulcanised rubber (which contains sulphur, and becomes brittle under the action of the chlorine).

The reaction which proceeds may be expressed thus: $\text{MnO}_2 + 2\text{NaCl} + 2\text{H}_2\text{SO}_4 = \text{MnSO}_4 + \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O} + \text{Cl}_2$. The method of preparation of Cl_2 from manganese peroxide and hydrochloric acid was discovered by Scheele, and from sodium chloride by Berthollet.

⁵ The reaction of hydrochloric acid upon bleaching powder gives chlorine without the aid of heat, $\text{CaCl}_2\text{O}_2 + 4\text{HCl} = \text{CaCl}_2 + 2\text{H}_2\text{O} + 2\text{Cl}_2$, and is therefore also used for the preparation of chlorine. This reaction is very violent if all the acid is added at once; it should be poured in drop by drop. C. Winkler proposed to mix bleaching powder with one quarter of its weight of burnt and powdered gypsum, and having damped the mixture with water, to press and cut it up into cubes and dry at the ordinary temperature. These cubes can be used for the preparation of chlorine in the same apparatus as that used for the evolution of hydrogen and carbonic anhydride—the disengagement of the chlorine proceeds uniformly.

A mixture of potassium dichromate and hydrochloric acid evolves chlorine perfectly free from oxygen (V. Meyer and Langer). Graebe (1902) showed that the gradual addition of hydrochloric acid (360 grms. of sp. gr. 1.17) to permanganate of potassium (50 grms.) gives a uniform stream of chlorine, exactly according to the equation, $\text{KMnO}_4 + 8\text{HCl} = \text{KCl} + \text{MnCl}_2 + 4\text{H}_2\text{O} + 5\text{Cl}$.

⁶ Chlorine is manufactured on a **large scale** from manganese peroxide and hydrochloric acid. It is most conveniently prepared in the apparatus shown in fig. 76, which consists of a three-necked earthenware vessel, the central orifice of which is the largest. A clay or lead funnel, furnished with a number of orifices, is placed in the central wide neck of the vessel. Roughly ground lumps of natural manganese peroxide are placed in the funnel, which is then closed by the cover N, and luted with clay. One orifice is closed by a clay stopper, and is used for the introduction of the hydrochloric acid and the withdrawal of the residues. The chlorine disengaged passes along a leaden gas-conducting tube fixed in the other orifice. A row of these vessels is surrounded by a water-bath to ensure their being uniformly heated. Manganese chloride is found in the residue. In Weldon's process lime is added to the acid solution of manganese chloride. A double decomposition takes place, resulting in the formation of manganous hydroxide and calcium chloride. When the insoluble manganous hydroxide has settled, a further excess of milk of lime is added (to make a

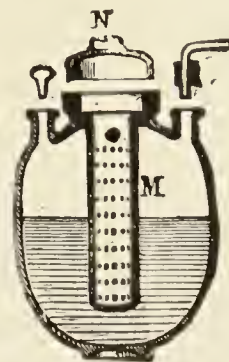


FIG. 76.—Clay retort for the preparation of chlorine on a large scale.

Chlorine is a **gas** of a yellowish-green colour, and has a very suffocating and characteristic odour. On lowering the temperature to -50° or increasing the pressure to six atmospheres (at 0°) chlorine condenses⁷ into a liquid which has a yellowish-green colour, a density of 1.4, and boils at -34° and solidifies about -100° . The density and atomic weight of chlorine are 35.5 times greater than those of hydrogen, hence the molecule contains Cl_2 .⁸ At 0° one volume of water dissolves about $1\frac{1}{2}$ volume of chlorine, at 10° about 3 volumes, at 50° again $1\frac{1}{2}$ volume.⁹ Such a solution of chlorine is termed chlorine water, and is employed in a diluted form in medicine and as a laboratory reagent. It is prepared by passing chlorine through a series of Woulfe's bottles or into an inverted retort filled with water. Under the action of light, chlorine water gives oxygen and hydrochloric acid. At 0° a saturated solution of chlorine yields a crystallo-hydrate, $\text{Cl}_2, 8\text{H}_2\text{O}$, which readily splits up into chlorine and water when heated, so that if

mixture $2\text{Mn}(\text{OH})_2 + \text{CaO} + x\text{CaCl}_2$, which are found by experiment to be the best proportions), and then air is forced through the mixture. The hydroxide is thus converted from a colourless to a brown substance, containing peroxide, MnO_2 , and oxide of manganese, Mn_2O_3 . This is due to the manganous oxide absorbing oxygen from the air. Under the action of hydrochloric acid this mixture evolves chlorine, because, of all the compounds of chlorine and manganese, the chloride MnCl_2 is the only one which is stable (see note 3). Thus one and the same mass of manganese may be repeatedly used for the preparation of chlorine. The same result is attained in other ways. If manganous oxide is subjected to the action of oxides of nitrogen and air (Coleman's process), manganese nitrate is formed, which at a red heat gives oxides of nitrogen (which are again used in the process) and manganese peroxide, which is thus renewed for the fresh evolution of chlorine.

⁷ Davy and Faraday liquefied chlorine in 1823 by heating the crystallo-hydrate, $\text{Cl}_2, 8\text{H}_2\text{O}$, in a bent tube (as with NH_3), surrounded by warm water, while the other end of the tube was immersed in a freezing mixture. Melsens condensed chlorine in freshly burnt charcoal (placed in a glass tube), which when cold absorbs an equal weight of chlorine. The tube was then fused up, the bent end cooled, and the charcoal heated, by which means the chlorine was expelled from the charcoal, and the pressure increased, as must be done in order to liquefy the gas.

⁸ V. Meyer and Langer (1885) having remarked that at 1400° the density of chlorine (taking its expansion as equal to that of nitrogen) is 29, consider that the molecules of chlorine partially split up and give molecules Cl , but it might be maintained that the decrease in density observed only depends on the increase of the coefficient of expansion.

⁹ The equilibrium between chlorine and steam as gases and between water, liquid chlorine, ice, and the solid crystallo-hydrate of chlorine, is evidently very complex. Gibbs, Guldberg (1870), and others gave a theory for similar states of equilibrium (strictly speaking phases), which was afterwards developed by Roozeboom (1887); but it would be inopportune here to enter into its details, which belong to the province of physical and theoretical chemistry. It will be sufficient in the first place to mention that there is now no doubt (according to the theory of heat, and the direct observations of Ramsay and Young) that the vapour pressures at one and the same temperature are different for the liquid and solid states of substances; secondly, to call attention to the following note; and, thirdly, to state that, in the presence of the crystallo-hydrate, water between 0.24° and $+28.7^{\circ}$ (when the hydrate and a solution may occur simultaneously) dissolves an amount of chlorine different from that dissolved in the absence of the crystallo-hydrate.

it be sealed up in a tube and heated to 35° , two layers of liquid are formed—a lower stratum of chlorine containing a small quantity of water, and an upper stratum of water containing a small quantity of chlorine.¹⁰

Chlorine explodes **with hydrogen**, if a mixture of equal volumes be exposed to the direct action of the sun's rays¹¹ or brought into contact with spongy platinum or a strongly heated substance, or subjected to the action of an electric spark. The explosion in this case takes place for exactly the same reasons—i.e., the evolution of heat and expansion of the resultant product—as in the case of detonating gas (Chap. III.). Diffused light acts in the same way, but slowly, whilst direct sunlight causes an explosion.¹² The hydrochloric acid gas produced by the

¹⁰ According to Faraday's data the hydrate of chlorine contains $\text{Cl}_2, 10\text{H}_2\text{O}$, but Roozeboom (1885) showed that it is poorer in water and has the composition $\text{Cl}_2, 8\text{H}_2\text{O}$. At first small, almost colourless, crystals are obtained, but they gradually form (if the temperature be below their critical point 28.7° , above which they do not exist) large yellow crystals, like those of potassium chromate. The specific gravity is 1.23. The hydrate is formed if there is more chlorine in a solution than it is able to dissolve under the dissociation pressure corresponding with a given temperature. *In the presence of the hydrate* the percentage amount of chlorine is 0.5 at 0° , 0.9 at 9° , and 1.82 at 20° . At temperatures below 9° the solubility is dependent on the formation of the hydrate; whilst at higher temperatures under the ordinary pressure the hydrate cannot be formed, and the solubility of chlorine falls, as it does for all gases (Chap. I.). If the crystallo-hydrate is not formed, then below 9° the solubility follows the same rule (at 6° , 1.07 per cent. Cl_2 , and at 9° , 0.95 per cent.). According to Roozeboom, the chlorine evolved by the hydrate presents the following dissociation pressures: 249 mm. at 0° , 398 at 4° , 620 at 8° , 797 at 10° , and 1,400 mm. at 14° . In this case a portion of the crystallo-hydrate remains solid. At 9.6° the pressure of dissociation is equal to the atmospheric pressure. At a higher pressure the crystallo-hydrate may form at temperatures above 9° and up to 28.7° , when the vapour pressure of the hydrate equals the pressure of the chlorine. It is evident that the equilibrium which is established is on the one hand a case of a complex heterogeneous system, and on the other hand a case of the solution of solid and gaseous substances in water.

The crystallo-hydrate or chlorine water must be kept in the dark, or the access of light prevented by coloured glass, otherwise oxygen is evolved and hydrochloric acid formed.

¹¹ The chemical action of light on a mixture of chlorine and hydrogen was discovered by Gay-Lussac and Thénard (1809). It has been investigated by many savants, and especially by Draper, Bunsen, and Roscoe. Electric or magnesium light, or the light emitted by the combustion of carbon bisulphide in nitric oxide, and actinic light in general, acts in proportion to its intensity, in the same manner as sunlight. At temperatures below -12° , light no longer brings about reaction, or at all events does not give an explosion. It was long supposed that chlorine that had been subjected to the action of light was afterwards able to act on hydrogen in the dark, but it was shown that this only takes place with moist chlorine, and depends on the formation of oxides of chlorine. The presence of foreign gases, and even of excess of chlorine or of hydrogen, very much enfeebles the explosion, and the experiment is therefore conducted with a detonating mixture prepared by the action of an electric current on a strong solution (sp. gr. 1.15) of hydrochloric acid, in which case the water is not decomposed—that is, no oxygen becomes mixed with the chlorine.

¹² The quantity of chlorine and hydrogen which combine is proportional to the intensity of the light—not of all the rays, but only of those so-called chemical (actinic) rays which

reaction of chlorine on hydrogen occupies (at the original temperature and pressure) a volume equal to the sum of the original volumes; that is, a reaction of substitution here takes place: $\text{H}_2 + \text{Cl}_2 = 2\text{HCl}$. In this reaction twenty-two thousand heat units are evolved for one part by weight (1 gram) of hydrogen.¹³

These relations show that the affinity of chlorine for hydrogen is very great and analogous to that between hydrogen and oxygen. Thus,¹⁴ on the one hand by passing a mixture of steam and chlorine through a red-hot tube, or by exposing water and chlorine to the sunlight, oxygen is disengaged, while on the other hand, as we saw above, oxygen in many cases displaces chlorine from its compound with

produce chemical action. Hence a mixture of chlorine and hydrogen, when exposed to the action of light in vessels of given capacity and surface, may be employed as an actinometer. Investigations of this kind (photo-chemical) showed that chemical action is chiefly limited to the violet end of the spectrum, and that even the invisible ultra-violet rays produce this action. A colourless gas flame contains no chemically active rays; the flame coloured green by a salt of copper evinces more chemical action than the colourless flame, but the flame coloured bright yellow by salts of sodium has no more chemical action than that of the colourless flame.

As the chemical action of light becomes evident in plants, photography, the bleaching of tissues, and the fading of colours in the sunlight, and as a means for studying the phenomenon is given in the reaction of chlorine on hydrogen, this subject has been the most fully investigated in **photo-chemistry**. The researches of Bunsen and Roscoe in the fifties and sixties form the basis of our knowledge of this subject. Their actinometer contains hydrogen and chlorine, and is surrounded by a solution of chlorine in water. The hydrochloric acid is absorbed as it forms, and therefore the variation in volume indicates the progress of the combination. The action of light proved, as might have been expected, to be proportional to the time of exposure and intensity of the light, so that it was possible to conduct detailed photometrical investigations respecting the time of day and season of the year, various sources of light, its absorption, &c. This subject is considered in detail in photo-chemistry.

As much heat is evolved in the reaction of chlorine on hydrogen, and as this reaction, being exothermal, may proceed by itself, the action of light is essentially the same as that of heat—that is, it brings the chlorine and hydrogen into the condition necessary for the reaction—it, as we may say, disturbs the original equilibrium; this is the work done by the luminous energy. It seems to me that the action of light on the mixed gases should be understood in this sense, as Pringsheim (1877) pointed out.

¹³ In the formation of steam (from one part by weight [1 gram] of hydrogen) 29,000 heat units are evolved. The following are the quantities of heat (thousands of units) evolved in the formation of various other *corresponding* compounds of oxygen and of chlorine (from Thomsen's, and, for Na_2O , Beketoff's results):

{ 2NaCl, 195;	CaCl ₂ , 170;	HgCl ₂ , 63;	2AgCl, 59.
{ Na ₂ O, 100;	CaO, 131;	HgO, 42;	Ag ₂ O, 6.
{ 2AsCl ₃ , 143;	2PCl ₅ , 210;	CCl ₄ , 21;	2HCl, 44 (gas).
{ As ₂ O ₃ , 155;	P ₂ O ₅ , 370;	CO ₂ , 97;	H ₂ O, 58 (gas).

With the first four elements the formation of the chlorine compound gives the more heat, and with the four following the formation of the oxygen compound evolves the greater amount of heat. The first four chlorides are true salts formed from HCl and the oxide, whilst the remainder have other properties, as is seen from the fact that they are not formed from hydrochloric acid and the oxide, but give hydrochloric acid with water.

¹⁴ This has been already pointed out in Chap. III., note 5.

hydrogen, and therefore the reaction, $\text{H}_2\text{O} + \text{Cl}_2 \rightleftharpoons 2\text{HCl} + \text{O}$, belongs to the class of reversible reactions, and hydrogen will distribute itself between oxygen and chlorine. This determines the relation of Cl to substances containing hydrogen and its reactions in the presence of water, to which we shall turn our attention after having pointed out the relation of chlorine to other elements.

Many **metals** when brought into contact with chlorine immediately combine with it, and form metallic chlorides corresponding with hydrogen chloride and with the oxide of the metal taken. This combination may proceed rapidly with the evolution of heat and light; that is, metals are able to burn in chlorine. Thus, for example, sodium¹⁵ burns in chlorine, synthesising common salt. Metals in the form of powder burn without the aid of heat, and become highly incandescent in the process; for instance, antimony, which is a metal readily convertible into a powder.¹⁶ Even such metals as gold and platinum,¹⁷ which do not combine directly with oxygen, and give very unstable compounds with it, unite directly with chlorine to form metallic chlorides. Either chlorine water or aqua regia may be employed for this purpose instead of gaseous chlorine. These dissolve gold and platinum, converting them into metallic chlorides. **Aqua regia** is a mixture of 1 part of nitric acid with 2 to 3 parts of hydrochloric acid.^{17a} This mixture converts into soluble chlorides, not only those metals which are acted on by hydrochloric and nitric acids, but also gold and platinum, which are insoluble in either acid separately. This action of aqua regia depends on the fact that nitric acid in acting

¹⁵ Sodium remains unaltered in perfectly dry chlorine at the ordinary temperature, and even when slightly warmed; but the combination is exceedingly violent at a red heat.

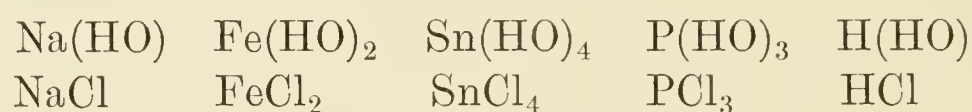
¹⁶ An instructive experiment on combustion in chlorine may be conducted as follows: leaves of Dutch metal (used instead of gold for gilding) are placed in a glass globe, and a gas-conducting tube furnished with a glass cock placed in the cork closing it, the air being then pumped out of the globe. The gas-conducting tube is then connected with a vessel containing chlorine, and the cock opened; the chlorine rushes in, and the metallic leaves are consumed.

¹⁷ The behaviour of platinum to chlorine at a high temperature (1400°) is very remarkable, because platinous chloride, PtCl_2 , is then formed, whilst this substance decomposes at a much lower temperature into chlorine and platinum. Hence, when chlorine comes into contact with platinum at such high temperatures, it forms fumes of platinous chloride, and these on cooling decompose, with the liberation of platinum, so that the phenomenon appears to be dependent on the volatility of platinum. Deville proved the formation of platinous chloride by inserting a cold tube inside a red-hot one (as in the experiment on carbonic oxide). However, V. Meyer was able to observe the density of chlorine in a platinum vessel at 1690° , at which temperature chlorine does not exert this action on platinum, or at least only to an insignificant degree.

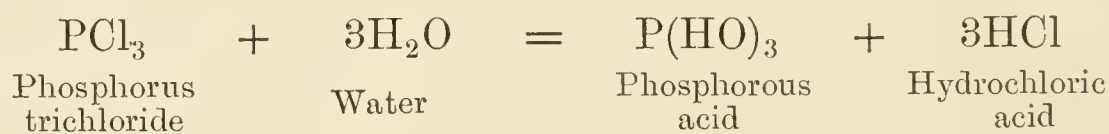
^{17a} Geber, the Arabian alchemist of the middle ages, showed that when a mixture of nitre and common salt is distilled in oil of vitriol it gives **aqua regia**, which dissolves gold. Chlorine is the active agent in aqua regia.

on hydrochloric acid evolves chlorine. If the chlorine evolved be transferred to a metal, then a fresh quantity is formed from the remaining acids and also combines with the metal.¹⁸ Thus the aqua regia acts by virtue of the chlorine which it contains and disengages.

The majority of **non-metals** also react directly on chlorine; hot sulphur and phosphorus burn in it and combine with it at the ordinary temperature. Only nitrogen, carbon, and oxygen do not combine directly with it. The chlorine compounds formed by the non-metals—for instance, phosphorus trichloride, PCl_3 , and sulphurous chloride, &c., have not the properties of salts, but correspond, as we shall afterwards see more fully, to acid anhydrides and acids; for example, PCl_3 —to phosphorous acid, $\text{P}(\text{OH})_3$:



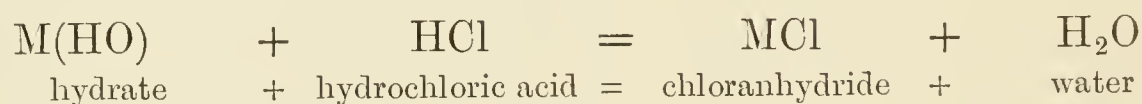
As the above-mentioned relation in composition---i.e., substitution of Cl by the aqueous residue---exists between many chloride compounds and their corresponding hydrates, and as furthermore some (acid) hydrates are obtained from chlorine compounds by the action of water, for instance,



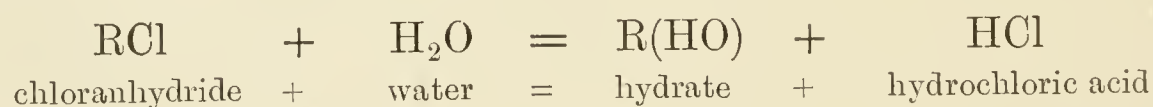
whilst other chlorine compounds are formed from hydroxides and hydrochloric acid, with the liberation of water, for example,



we endeavour to express this intimate connection between the hydrates and chlorine compounds by calling the latter **chloranhydrides**. In general terms, if the hydrate be basic,



and if the hydrate ROH be acid, then,



¹⁸ When left exposed to the air aqua regia disengages chlorine, and afterwards it no longer acts on gold. Gay-Lussac, in explaining the action of aqua regia, showed that when heated it evolves, besides chlorine, the vapours of two chloranhydrides—that of nitric acid, NO_2Cl (nitric acid, NO_2OH , in which HO is replaced by chlorine; see chapter on Phosphorus), and that of nitrous acid, NOCl —but these do not act on gold. The formation of aqua regia may therefore be expressed by: $4\text{NHO}_3 + 8\text{HCl} = 2\text{NO}_2\text{Cl} + 2\text{NOCl} + 6\text{H}_2\text{O} + 2\text{Cl}_2$. The formation of the chlorides NO_2Cl and NOCl is explained by the fact that the nitric acid is deoxidised, gives the oxides NO and NO_2 , and these combine directly with chlorine to form the above anhydrides.

The chloranhydrides MCl corresponding with the bases are evidently metallic chlorides or salts corresponding with HCl . In this manner a distinct equivalency is noticed between the compounds of chlorine and the so-called hydroxyl radicle (HO), which is also expressed in the analogy existing between chlorine, Cl_2 , and hydrogen peroxide $(HO)_2$; for instance, both oxidise, bleach, &c.

As regards the chloranhydrides corresponding with acids and non-metals, these bear but little resemblance to metallic salts. They are nearly all volatile, and have a powerful suffocating smell which irritates the eyes and respiratory organs. They react on water like many anhydrides of the acids, with the evolution of heat and liberation of hydrochloric acid, forming acid hydrates. There are many intermediate chlorine compounds between true saline metallic chlorides like sodium chloride and true acid chloranhydrides, like PCl_3 , just as there are all degrees of transition between bases and acids. Acid chloranhydrides are not only obtained from chlorine and non-metals, but also from many lower oxides, by the aid of chlorine. Thus, for example, CO , NO , NO_2 , SO_2 , and other lower oxides which are capable of combining with oxygen, may also combine with a corresponding quantity of chlorine, $COCl_2$, $NOCl$, NO_2Cl , SO_2Cl_2 , &c., being obtained. They correspond with the hydrates $CO(OH)_2$, $NO(OH)$, $NO_2(OH)$, $SO_2(OH)_2$, &c., and with the anhydrides CO_2 , N_2O_3 , N_2O_5 , SO_3 , &c. Here we should notice two aspects of the question: (1) chlorine combines with that with which oxygen is able to combine, because it is in many respects as energetic as, if not more so than, oxygen, and replaces it in the proportion $Cl_2 : O$; (2) that highest limit of possible combination which is proper to a given element or grouping of elements is very easily and often attained by combination with chlorine. If phosphorus gives PCl_3 and PCl_5 , it is evident that PCl_5 is the higher form of combination compared with PCl_3 . To the form PCl_5 , or in general PX_5 , correspond PH_4I , $PO(OH)_3$, $POCl_3$, &c. If chlorine does not always directly give compounds of the highest possible forms for a given element, then generally the lower forms combine with it in order to reach or approach the limit. This is particularly clear in hydrocarbons, where we see the limit, C_nH_{2n+2} , very distinctly. The unsaturated hydrocarbons are sometimes able to combine with chlorine with the greatest ease, and thus reach the limiting state. Thus ethylene, C_2H_4 , combines with Cl_2 , forming the so-called Dutch liquid or ethylene chloride, $C_2H_4Cl_2$, because it then reaches the limit C_nX_{2n+2} . In this and all similar cases the combined chlorine is able by reactions of substitution to give more or less easily a hydroxide and a whole

series of other derivatives. Thus a hydroxide called glycol, $\text{C}_2\text{H}_4(\text{OH})_2$, is obtained from $\text{C}_2\text{H}_4\text{Cl}_2$.

Chlorine in the presence of water very often acts directly as an **oxidising agent**. A substance A combines with chlorine and gives, for example, ACl_2 , and this in turn a hydroxide, $\text{A}(\text{OH})_2$, which on losing water forms AO . Here the chlorine has oxidised the substance A. This frequently happens in the simultaneous action of water and chlorine: $\text{A} + \text{H}_2\text{O} + \text{Cl}_2 = 2\text{HCl} + \text{AO}$. Examples of this oxidising action of chlorine may frequently be observed both in practical chemistry and in technical processes. Thus, for instance, chlorine in the presence of water oxidises sulphur and metallic sulphides. In this case the sulphur is converted into sulphuric acid, and the chlorine into hydrochloric acid, or a metallic chloride if a metallic sulphide be taken. A mixture of carbonic oxide and chlorine passed into water gives carbonic anhydride and hydrochloric acid: $\text{CO} + \text{Cl}_2 + \text{H}_2\text{O} = \text{CO}_2 + 2\text{HCl}$. Sulphurous anhydride is oxidised by chlorine in the presence of water into sulphuric acid, just as it is by the action of nitric acid: $\text{SO}_2 + 2\text{H}_2\text{O} + \text{Cl}_2 = \text{H}_2\text{SO}_4 + 2\text{HCl}$.

The oxidising action of chlorine in the presence of water is taken advantage of in practice for the rapid **bleaching of tissues** and fibres. The colouring matter of the fibres is altered by oxidation and converted into a colourless substance.¹⁹

The power of chlorine for combination is intimately connected with its capacity for substitution, because, according to the law of substitution, if chlorine combines with hydrogen, then it also replaces hydrogen, and, furthermore, the combination and substitution are accomplished in the same quantities. Therefore the **atom of chlorine** which combines with the atom of hydrogen is also able **to replace the atom of hydrogen**. This property of chlorine illustrates the application of the law of

¹⁹ But the chlorine afterwards acts on the tissue itself. Bleaching by means of chlorine therefore requires a certain amount of technical skill in order that the chlorine should not act on the fibres themselves, but that its action should be limited to the colouring matter only. The fibre for making writing paper, for instance, is bleached in this manner. The bleaching property of chlorine was discovered by Berthollet, and forms an important acquisition to the arts, because it has in the majority of cases replaced what was before the universal method of bleaching—namely, exposure to the sun of the fabrics damped with water—which is still employed for linens, &c. Time and great trouble, and therefore money also, have been saved by this change. Ozone and peroxide of hydrogen also bleach tissues. As the action of peroxide of hydrogen is easily controlled by taking a weak solution, and as it has hardly any action upon the tissues themselves, it is replacing chlorine more and more as a bleaching agent. The oxidising property of chlorine is apparent in destroying the majority of organic tissues, proving fatal to organisms. This action of chlorine is taken advantage of in quarantine stations. But the simple fumigation by chlorine must be carried on with great care in dwelling-places, because chlorine discharged into the atmosphere renders it injurious to health.

substitution in clear and historically important examples, and reactions of this kind explain those **indirect methods** of the formation of many substances which we have often mentioned, and to which recourse is had in many cases in chemistry. Thus chlorine does not act on carbon,²⁰ oxygen, or nitrogen, but nevertheless its compounds with these elements may be obtained by the indirect method of the substitution of hydrogen by chlorine.

As chlorine easily combines with hydrogen, and does not act on carbon, it decomposes hydrocarbons (and many of their derivatives) at a high temperature, depriving them of their hydrogen and liberating the carbon, as is clearly seen, for example, when a lighted candle is placed in a vessel containing chlorine. The flame becomes smaller, but continues for a certain time, a large amount of soot being obtained, and hydrochloric acid being formed. In this case the gaseous and incandescent substances of the flame are decomposed by the chlorine, the hydrogen combines with it, and the carbon is disengaged as soot.²¹ This action of chlorine on hydrocarbons proceeds otherwise at low temperatures, as we will now consider.

A very important epoch in the history of chemistry was inaugurated by the discovery of Dumas and Laurent that chlorine is able to displace and **replace hydrogen**. This discovery is important from the fact that chlorine proved to be an element which combines with great ease simultaneously with both the hydrogen and the element with which the hydrogen was combined. This clearly proved that there is no opposite polarity between elements forming stable compounds. Chlorine does not combine with hydrogen because it has opposite properties, as was previously stated by Dumas and Laurent, who accounted hydrogen to be electro-positive and chlorine electro-negative ; this is not the reason of their combining together, for the same chlorine which combines with hydrogen is also able to replace it without altering many of the properties of the resultant substance. This substitution of hydrogen by chlorine is termed **metalepsis**. The mechanism of this substitution follows a very uniform course. If we take a hydrogen compound, preferably a hydrocarbon, and allow chlorine to act directly on it, there is produced, on the one hand, hydrochloric acid, and, on the other,

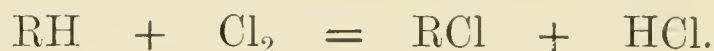
²⁰ A tendency of carbon to attract chlorine is evidenced in the immense absorption of chlorine by charcoal (note 7), but, so far as is at present known (if I am not mistaken, no one has tried the aid of light), no combination takes place between the chlorine and carbon.

²¹ The same reaction takes place under the action of oxygen, with the difference that it burns the carbon, which chlorine is not able to do. If chlorine and oxygen compete together at a high temperature, the oxygen will unite with the carbon, and the chlorine with the hydrogen.

a compound containing chlorine in the place of the hydrogen; so that the chlorine divides itself into two equal portions: one portion is evolved as hydrochloric acid, and the other portion takes the place of the hydrogen thus liberated. **Hence this metalepsis is always accompanied by the formation of hydrochloric acid.**²² The scheme of the process is as follows:



Or, generally—



The conditions under which metalepsis takes place are also very constant. In the dark, chlorine rarely acts on hydrogen compounds, but the action commences under the influence of light. The direct action of the sun's rays is particularly favourable to metalepsis. It is also remarkable that the presence of traces of certain substances,²³ especially of iodine, aluminium chloride, antimony chloride, &c., promotes the action. A trace of iodine added to the substance subjected to metalepsis often produces the same effect as sunlight.²⁴

If marsh gas is mixed with chlorine and the mixture ignited, the hydrogen is entirely taken up from the marsh gas and hydrochloric acid and carbon are formed, but there is no metalepsis.²⁵ But if a mixture

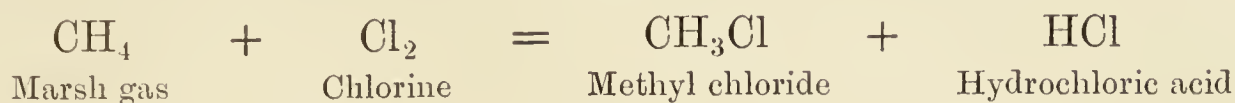
²² This division of chlorine into two portions may at the same time be taken as a clear confirmation of the conception of the molecule Cl_2 containing two atoms.

²³ Such carriers or media for the transference of chlorine and the halogens in general were long known to exist in iodine and antimonious chloride, and have been most fully studied by Gustavson and Friedel, of the Petroffsky Academy—the former with respect to aluminium bromide, and the latter with respect to aluminium chloride. Gustavson showed that if a trace of metallic aluminium be dissolved in bromine (it floats on bromine, and when combination takes place much heat and light are evolved), the latter becomes endowed with the property of entering into metalepsis, which it is not able to do of its own accord. When pure, for instance, it acts very slowly on benzene, C_6H_6 , but in the presence of a trace of aluminium bromide the reaction proceeds violently and easily, so that each drop of the hydrocarbon gives a mass of hydrobromic acid, and of the product of metalepsis. Gustavson showed that the *modus operandi* of this instructive reaction is based on the power of aluminium bromide to enter into combination with hydrocarbons and their derivatives. The details of this and all researches concerning the metalepsis of the hydrocarbons must be looked for in works on organic chemistry.

²⁴ As small admixtures of iodine, aluminium bromide, &c., aid the metalepsis of large quantities of a substance, just as nitric oxide aids the reaction of sulphurous anhydride on oxygen and water, so the principle is essentially the same in both cases. Effects of this kind (which should also be explained by a chemical reaction proceeding at the surfaces) only differ from true contact phenomena in that the latter are produced by solid bodies and are accomplished at their surfaces, whilst in the former all is in solution. Probably the action of iodine is founded on the formation of iodine chloride, which reacts more easily than chlorine.

²⁵ Metalepsis belongs to the category of delicate reactions—if it may be so expressed—as compared with the energetic reaction of combustion. Many cases of substitution are

of equal volumes of chlorine and marsh gas be exposed to the action of diffused light, then the greenish-yellow mixture will gradually become colourless, and hydrochloric acid and the first product of metalepsis—namely, methyl chloride—will be formed :



The volume of the mixture remains unaltered. The methyl chloride which is formed is a gas. If it be separated from the hydrochloric acid (it is soluble in acetic acid, in which hydrochloric acid is but sparingly soluble) and be again mixed with chlorine, it may be subjected to a further metalepsical substitution—the second atom of hydrogen may be substituted by chlorine, and a liquid substance, CH_2Cl_2 , called methylene chloride, obtained. In the same manner the substitution may be carried on still further, and CHCl_3 , or chloroform, and lastly carbon tetrachloride, CCl_4 , produced. Of these substances the best known and most widely used is chloroform, owing to its being formed from many organic substances (by the action of bleaching powder) and to its being used in medicine as an anæsthetic ; chloroform boils at 62° and carbon tetrachloride at 78° . They are both colourless odoriferous liquids, heavier than water. The progressive substitution of hydrogen by chlorine is thus evident, and it can be clearly seen that the double decompositions are accomplished between molecular quantities of the substances—that is, between equal volumes in a gaseous state.

It is evident that by ultimate metalepsis a corresponding carbon chloride may be obtained from any hydrocarbon—indeed, the number of chlorides of carbon, C_nCl_{2m} , already known is very large.

As a rule, the fundamental chemical characters of hydrocarbons are not changed by metalepsis ; that is, if a neutral substance is taken, then the product of metalepsis is also a neutral substance, or if an acid be taken the product of metalepsis also has acid properties. Even the crystalline form not infrequently remains unaltered after metalepsis. The metalepsis of acetic acid, $\text{CH}_3\cdot\text{COOH}$, is historically the most important. This acid contains three of the atoms of the hydrogen of marsh gas, the fourth being replaced by carboxyl, and therefore by the action of chlorine it gives three products of metalepsis (according to the amount of the chlorine and conditions under which the reaction

of this kind. Reactions of metalepsis are accompanied by an evolution of heat, but in a less quantity than that evolved in the formation of the resulting quantity of the halogen acids. Thus the reaction, $\text{C}_2\text{H}_6 + \text{Cl}_2 = \text{C}_2\text{H}_5\text{Cl} + \text{HCl}$, according to the data given by Thomsen, evolves about 20,000 heat units, whilst the formation of hydrochloric acid evolves 22,000 units.

takes place), mono-, di-, and tri-chloracetic acids— $\text{CH}_2\text{Cl}\cdot\text{COOH}$, $\text{CHCl}_2\cdot\text{COOH}$, and $\text{CCl}_3\cdot\text{COOH}$; these are all, like acetic acid, mono-basic. The resulting products of metalepsis, in containing an element which so easily acts on metals as chlorine, possess the possibility of attaining a further complexity of molecules of which the original hydrocarbon is often in no way capable. Thus on treating with an alkali (or first with a salt and then with an alkali, or with a basic oxide and water, &c.), the chlorine forms a salt with its metal, and the hydroxyl radicle takes the place of the chlorine—for example, $\text{CH}_3\cdot\text{OH}$ is obtained from CH_3Cl . By the action of metallic derivatives of hydrocarbons—for example, $(\text{CH}_3)_2\text{Zn}$, CH_3Na —the chlorine also gives a salt, and the hydrocarbon radicle—for instance, CH_3 —takes the place of the chlorine. In this, or in a similar manner, $\text{CH}_3\cdot\text{CH}_3$, or C_2H_6 is obtained from CH_3Cl and $\text{C}_6\text{H}_5\cdot\text{CH}_3$ from $\text{C}_6\text{H}_5\text{Cl}$. The products of metalepsis also often react on ammonia, forming hydrochloric acid (and thence NH_4Cl) and an amide, that is, the product of metalepsis in which the ammonia radicle, NH_2 , takes the place of chlorine. Thus, by means of metalepsical substitution, methods were found in chemistry for an artificial and general means of the formation of complex carbon compounds from more simple compounds which are often totally incapable of direct reaction. Besides which, this key opened the door of that secret edifice of complex organic compounds into which man had up to then feared to enter, supposing the hydrocarbon elements to be united only under the influence of those mystic forces acting in organisms.²⁶

It is not only hydrocarbons which are subject to **metalepsis**. Certain other hydrogen compounds, under the action of chlorine, also

²⁶ With the predominance of the representation of compound radicles (this doctrine dates from the time of Lavoisier and Gay-Lussac) in organic chemistry, it was a very important moment in its history when it became possible to gain an insight into the structure of the radicles themselves. It was clear, for instance, that ethyl, C_2H_5 , or the radicle of common alcohol, $\text{C}_2\text{H}_5\cdot\text{OH}$, passes, without changing, into a number of ethyl derivatives, but its relation to the still simpler hydrocarbons was not clear, and occupied the attention of science in the 'forties' and 'fifties.' Ethyl hydride, $\text{C}_2\text{H}_5\text{H} = \text{C}_2\text{H}_6$, being obtained, it was regarded as containing the same ethyl, just as methane, $\text{CH}_4 = \text{CH}_3\text{H}$, was considered as methyl hydride. Having obtained free methyl, $\text{CH}_3\text{CH}_3 = \text{C}_2\text{H}_6$, from it, it was considered as a derivative of methyl alcohol, CH_3OH , and as only isomeric with ethyl hydride. By means of the products of metalepsis it was proved that this is a case, not of isomerism, but of strict identity, and it therefore became clear that ethyl is methylated methyl, $\text{C}_2\text{H}_5 = \text{CH}_2\text{CH}_3$. In its time a still greater impetus was given by the study of the reactions of monochloracetic acid, $\text{CH}_2\text{Cl}\cdot\text{COOH}$, or $\text{CO}(\text{CH}_2\text{Cl})(\text{OH})$. It appeared that metalepsical chlorine, like the chlorine of chloranhydrides—for instance, of methyl chloride, CH_3Cl , or ethyl chloride, $\text{C}_2\text{H}_5\text{Cl}$ —is capable of substitution; for example, glycollic acid, $\text{CH}_2(\text{OH})(\text{CO}_2\text{H})$, or $\text{CO}(\text{CH}_2\cdot\text{OH})(\text{OH})$, was obtained from it, and it appeared that the OH in the group $\text{CH}_2(\text{OH})$ reacted like that in alcohols, and it became clear, therefore, that it was necessary to examine the radicles themselves by analysing them from the point of view of the bonds connecting the constituent atoms. Whence arose the present doctrine of the structure of the carbon compounds.

give corresponding chlorine derivatives in exactly the same manner ; for instance, ammonia, caustic potash, caustic lime, and a whole series of **alkaline** substances.²⁷ In fact, just as the hydrogen in marsh gas can be replaced by chlorine, forming methyl chloride, so the hydrogen in caustic potash, KHO, ammonia, NH₃, and calcium hydroxide, CaH₂O₂ or Ca(OH)₂, may be replaced by chlorine and give potassium hypochlorite, KClO, calcium hypochlorite, CaCl₂O₂, and the so-called chloride of nitrogen, NCl₃. For not only is the correlation in composition the same as in the substitution in marsh gas, but the whole mechanism of the reaction is the same. Here also two atoms of chlorine act : one takes the place of the hydrogen whilst the other is evolved as hydrochloric acid, only in the former case the hydrochloric acid evolved remained free, and in the latter, in presence of alkaline substances, it reacts on them. Thus, in the action of chlorine on caustic potash, the hydrochloric acid formed acts on a further quantity of caustic potash and gives potassium chloride and water, and therefore not only $\text{KHO} + \text{Cl}_2 = \text{HCl} + \text{KClO}$, but also $\text{KHO} + \text{HCl} = \text{H}_2\text{O} + \text{KCl}$, and the result of the two simultaneous actions will be $2\text{KHO} + \text{Cl}_2 = \text{H}_2\text{O} + \text{KCl} + \text{KClO}$.

The action of **chlorine on ammonia** may result either in the entire breaking down of the ammonia, with the evolution of gaseous nitrogen, or in a product of metalepsis (as with CH₄). With an excess of chlorine and the aid of heat the ammonia is decomposed, with the disengagement of free nitrogen.²⁸ This reaction evidently results

²⁷ By including many instances of the action of chlorine under metalepsis we not only explain the indirect formation of CCl₄, NCl₃, and Cl₂O by one method, but we also arrive at the fact that the reactions of the metalepsis of the hydrocarbons lose that exclusiveness which was often ascribed to them. Also by subjecting the chemical representations to the law of substitution we may predict metalepsis to be a particular case of a general law. It must be remembered, however, that the chlorine in all the products of metalepsis reacts more or less differently from the chlorine in chlorides. Thus, for instance, salts of silver, AgX, immediately give AgCl + MX with solutions of soluble chlorides, MCl, but this reaction proceeds very slowly with products of metalepsis. Without entering into the consideration of the velocity of reaction (which belongs to theoretical chemistry) I will only mention that the chlorine in the so-called 'complex' compounds (see Chapters XXII. and XXIII.), which is apparently combined with the metal, either does not react or reacts slowly with AgX, and so recalls metalepsical chlorine. The relations of this latter property cannot yet be considered as satisfactorily explained, but they are being worked at by many and present a peculiar interest. Owing to the complexity and incompleteness of the subject I have only referred to it in the last chapters of this work and have limited myself as far as possible to facts and analogies.

²⁸ This may be taken advantage of in the preparation of nitrogen. If a large excess of chlorine water be poured into a beaker, and a small quantity of a solution of ammonia be added, then, after shaking, nitrogen is evolved. If ammonia gas be passed through a fine orifice into a vessel containing chlorine, the reaction of the formation of nitrogen is accompanied by the emission of light and the appearance of a cloud of sal-ammoniac. In all these instances an excess of chlorine must be present.

in the formation of sal-ammoniac, $8\text{NH}_3 + 3\text{Cl}_2 = 6\text{NH}_4\text{Cl} + \text{N}_2$. But if the ammonium salt is in excess, the reaction takes the direction of the replacement of the hydrogen in the ammonia by chlorine. The principal result is that $\text{NH}_3 + 3\text{Cl}_2$ forms $\text{NCl}_3 + 3\text{HCl}$.²⁹ The resulting product of metalepsis, or **chloride of nitrogen**, NCl_3 , discovered by Dulong, is a liquid having the property of decomposing with excessive ease, not only when heated, but even under the action of mechanical influences, such as a blow or contact with certain solid substances. The explosion which accompanies the decomposition is due to the fact that the liquid chloride of nitrogen gives gaseous products, nitrogen and chlorine.^{29a}

²⁹ The hydrochloric acid formed combines with ammonia, and therefore the final result is: $4\text{NH}_3 + 3\text{Cl}_2 = \text{NCl}_3 + 3\text{NH}_4\text{Cl}$. The metalepsical reaction only takes place with an excess of ammonia or its salt. If bubbles of chlorine are passed through a fine tube into a vessel containing ammonia gas, each bubble gives rise to an explosion. If, however, chlorine is passed into a solution of ammonia, the reaction at first brings about the formation of nitrogen, because chloride of nitrogen acts on ammonia like chlorine. But when sal-ammoniac has begun to form, the reaction then directs itself towards the formation of chloride of nitrogen. The first action of chlorine on a solution of sal-ammoniac always causes the formation of chloride of nitrogen, which then reacts on ammonia thus: $\text{NCl}_3 + 4\text{NH}_3 = \text{N}_2 + 3\text{NH}_4\text{Cl}$. Therefore, so long as the liquid is alkaline from the presence of ammonia the chief product will be nitrogen. The reaction, $\text{NH}_4\text{Cl} + 3\text{Cl}_2 = \text{NCl}_3 + 4\text{HCl}$ is reversible; with a dilute solution it proceeds in the above-described direction (perhaps owing to the affinity of the hydrochloric acid for the excess of water), but with a strong solution of hydrochloric acid it takes the opposite direction (probably by virtue of the affinity of hydrochloric acid for ammonia). Therefore there must exist a very interesting case of equilibrium between ammonia, hydrochloric acid, chlorine, water, and chloride of nitrogen. The reaction $\text{NCl}_3 + 4\text{HCl} = \text{NH}_4\text{Cl} + 3\text{Cl}_2$ enabled Deville and Hautefeuille to determine the composition of chloride of nitrogen. When slowly decomposed by water, chloride of nitrogen gives, like a chloranhydride, nitrous acid or its anhydride, $2\text{NCl}_3 + 3\text{H}_2\text{O} = \text{N}_2\text{O}_3 + 6\text{HCl}$. From these observations it is evident that chloride of nitrogen presents great chemical interest, which is strengthened by its analogy with trichloride of phosphorus. The researches of F. F. Selivanoff (1891-94) prove that NCl_3 may be regarded as an ammonium derivative of hypochlorous acid. Chloride of nitrogen is decomposed by dilute sulphuric acid in the following manner: $\text{NCl}_3 + 3\text{H}_2\text{O} + \text{H}_2\text{SO}_4 = \text{NH}_4\text{HSO}_4 + 3\text{HClO}$. This reaction is reversible and is only complete when some substance, combining with HClO (for instance, succinimide) or decomposing it, is added to the liquid. This is partly understood from the fact that hypochlorous acid itself, HClO , may, according to the view held in this book, be regarded as the product of the metalepsis of water, and consequently bears the same relation to NCl_3 as H_2O does to NH_3 , or as RHO to RNH_2 , R_2NH , and R_3N —that is to say, NCl_3 corresponds, as an ammonium derivative, with ClOH and Cl_2 in exactly the same manner as NR_3 corresponds with ROH and R_2 . Selivanoff obtained, investigated, and classified many of the compounds NR_2Cl and NRCl_2 , where R is a residue of an organic acid or alcohol, and showed their difference from the chloranhydrides, and thus supplemented the history of chloride of nitrogen, which is the simplest of the amides containing chlorine— NR_3 where R is fully substituted by chlorine.

^{29a} In preparing NCl_3 every precaution must be used to guard against an explosion, and care should be taken that the NCl_3 remains under a layer of water. Whenever an ammoniacal substance comes into contact with chlorine great care must be taken, because it may lead to the formation of such products, and a very dangerous explosion ensue. The liquid product of the metalepsis of ammonia may be most safely pre-

Chloride of nitrogen is a yellow oily liquid of sp. gr. 1.65, which boils at 71°, and breaks up into $N + Cl_3$ at 97°. The contact of phosphorus, turpentine, indiarubber, &c., causes an explosion, which is sometimes so violent that a small drop will pierce a thick board. The great ease with which chloride of nitrogen decomposes is dependent upon the fact that it is formed with an absorption of heat, which it evolves when decomposed, to the amount of about 38,000 heat units for NCl_3 , as Deville and Hautefeuille determined.

Chlorine, when absorbed by a solution of caustic soda (and also of other alkalies) at the ordinary temperature, causes the replacement of the hydrogen in the caustic soda by the chlorine, with the formation of sodium chloride by the hydrochloric acid, so that the reaction may be represented in two phases, as described above, or, taken as a whole, by the equation: $2NaHO + Cl_2 = NaCl + NaClO + H_2O$. The resultant solution contains $NaClO$ and is termed 'eau de Javelle.'^{29b} An exactly similar reaction takes place when chlorine is passed over dry hydrate of lime at the ordinary temperature: $2Ca(HO)_2 + 2Cl_2 = CaCl_2O_2 + CaCl_2 + 2H_2O$. A mixture of the product of metalepsis with calcium chloride is obtained. This mixture is employed in practice on a large scale, and is termed **bleaching powder**, owing to its acting, especially when mixed with acids, as a bleaching agent on tissues, in which respect it hence resembles chlorine. It is, however, preferable to chlorine, because the destructive action of the chlorine can be moderated in this case, and because it is much more convenient to deal with a solid substance than with gaseous chlorine. Bleaching powder is also called **chloride of lime**, because it is obtained from chlorine

pared in the form of small drops by the action of a galvanic current on a slightly warm solution of sal-ammoniac; chlorine is then evolved at the anode, and this chlorine acting on the ammonia gradually forms the product of metalepsis, which floats on the surface of the liquid (being carried up by the gas), and if a layer of turpentine be poured on to it these small drops, on coming into contact with the turpentine, give feeble explosions, which are in no way dangerous owing to the small mass of the substance formed. Drops of chloride of nitrogen may with great caution be collected for investigation in the following manner. The neck of a funnel is immersed in a basin containing mercury, and first a saturated solution of common salt is poured into the funnel, and above it a solution of sal-ammoniac in 9 parts of water. Chlorine is then slowly passed through the solutions, when drops of chloride of nitrogen fall into the salt water. Hentschel (1897) proceeded as follows in order to prepare a solution of NCl_3 in benzene. He carefully mixed a solution of bleaching powder with as much hydrochloric acid as would not lead to the formation of gas on the addition of sal-ammoniac, and then added a solution of NH_4Cl and benzene. By constant shaking the NCl_3 formed, dissolved in the benzene, and floated on the surface. Such a solution may be kept without danger in the dark.

^{29b} Solutions of hypochlorite of sodium can only be kept without change (without forming $NaClO_3$) in the presence of an excess of alkali and in the dark (Graebe).

and hydrate of lime, and contains ³⁰ both these substances. It may be prepared in the laboratory by passing a current of chlorine through a cold mixture of water and lime (milk of lime). The mixture must be kept cold, as otherwise $3\text{Ca}(\text{ClO})_2$ passes into $2\text{CaCl}_2 + \text{Ca}(\text{ClO}_3)_2$. In the manufacture of bleaching powder in large quantities at chemical works, the purest possible slaked lime is taken and laid in a thin layer in large flat chambers, M (whose walls are made of Yorkshire flags or tarred wood, on which chlorine has no action), and into which chlorine gas is introduced by lead tubes. The distribution of the plant is shown in the annexed drawing (fig. 77).

The products of the metalepsis of alkaline hydrates, NaClO and $\text{Ca}(\text{ClO})_2$, which are present in solutions of 'Javelle salt' and bleaching powder (they are not obtained free from metallic chlorides), must be counted as salts, because their metals are capable of substitution. But

³⁰ Quicklime, CaO (or calcium carbonate, CaCO_3), does not absorb chlorine when cold, but at a red heat, in a current of chlorine, it forms calcium chloride, with the evolution of oxygen. (This was confirmed in 1893 by Wells, at Oxford.) This reaction corresponds with the decomposing action of chlorine on methane, ammonia, and water. Slaked lime (calcium hydroxide, CaH_2O_2) also, when dry, does not absorb chlorine at 100° . The absorption proceeds at the ordinary temperature (below 40°). The dry mass thus obtained contains not less than three equivalents of calcium hydroxide to four of chlorine, so that its composition is $[\text{Ca}(\text{HO})_2]_3\text{Cl}_4$. In all probability a simple absorption of chlorine by the lime at first takes place in this case, as may be seen from the fact that even carbonic anhydride, when acting on the dry mass obtained as above, disengages all the chlorine from it, leaving only calcium carbonate. But if the bleaching powder be obtained by a wet method, or if it be dissolved in water (in which it is very soluble), and carbonic anhydride be passed into it, chlorine will no longer be disengaged, but its oxide, Cl_2O , into which only half of the chlorine is converted, the other half remaining in the liquid as calcium chloride. From this it may be inferred that calcium chloride is formed by the action of water on bleaching powder, and this is proved to be the case by the fact that small quantities of water extract a considerable amount of calcium chloride from bleaching powder. If a large quantity of water acts on bleaching powder an excess of calcium hydroxide remains, a portion of which is not subjected to change. The action of the water may be expressed by the following formulæ: From the dry mass, $\text{Ca}_3(\text{HO})_6\text{Cl}_4$ there is formed lime, $\text{Ca}(\text{HO})_2$, calcium chloride, CaCl_2 , and a saline substance, $\text{Ca}(\text{ClO})_2$: $\text{Ca}_3\text{H}_6\text{O}_6\text{Cl}_4 = \text{CaH}_2\text{O}_2 + \text{CaCl}_2\text{O}_2 + \text{CaCl}_2 + 2\text{H}_2\text{O}$. The resulting substances are not equally soluble; water first extracts the calcium chloride, which is the most soluble, then the compound $\text{Ca}(\text{ClO})_2$, calcium hydroxide being ultimately left. A mixture of calcium chloride and hypochlorite passes into solution. On evaporation there remains $\text{Ca}_2\text{O}_2\text{Cl}_4, 3\text{H}_2\text{O}$. The dry bleaching powder does not absorb more chlorine, but the solution is able to absorb it in considerable quantity. If the liquid be boiled, a considerable amount of chlorine monoxide is evolved. After this, calcium chloride alone remains in solution, and the decomposition may be expressed as follows: $\text{CaCl}_2 + \text{CaCl}_2\text{O}_2 + 2\text{Cl}_2 = 2\text{CaCl}_2 + 2\text{Cl}_2\text{O}$. Chlorine monoxide may be prepared in this manner. As bleaching salts in solution are used for bleaching fibres and tissues, attention should be turned to the fact that such solutions may be obtained with comparative ease by means of an electric current, for at low temperatures (up to 25°) bleaching salts are formed at the anode in the electrolysis of chlorides. Thus a 10 per cent. of NaCl can easily give solutions containing 1 per cent. of active chlorine with a sufficiently large anode surface and in suitable apparatus. This corresponds to the requirements of many bleaching establishments, where this method is frequently employed.

the hydrate, HClO , corresponding with these salts, or **hypochlorous acid**, is not obtained in a free or pure state, for two reasons: in the first place, because this hydrate, as a very feeble acid, splits up (like H_2CO_3 or HNO_3) into water and the anhydride, or **chlorine monoxide**, $\text{Cl}_2\text{O} = 2\text{HClO} - \text{H}_2\text{O}$; and, in the second place, because, in a number of instances, it evolves oxygen with great facility, forming hydrochloric acid: $\text{HClO} = \text{HCl} + \text{O}$. Both hypochlorous acid and chlorine monoxide may be regarded as products of the metalepsis of water, because HOH corresponds with ClOH and ClOCl . Hence in many instances bleaching salts (a mixture of hypochlorites and chlorides) break up, with the evolution of (1) *chlorine*, under the action of an excess of a powerful acid capable of evolving hydrochloric acid from sodium or calcium chlorides, and this takes place most simply under the action of hydrochloric acid itself, because $\text{NaCl} + \text{NaClO} + 3\text{HCl}$

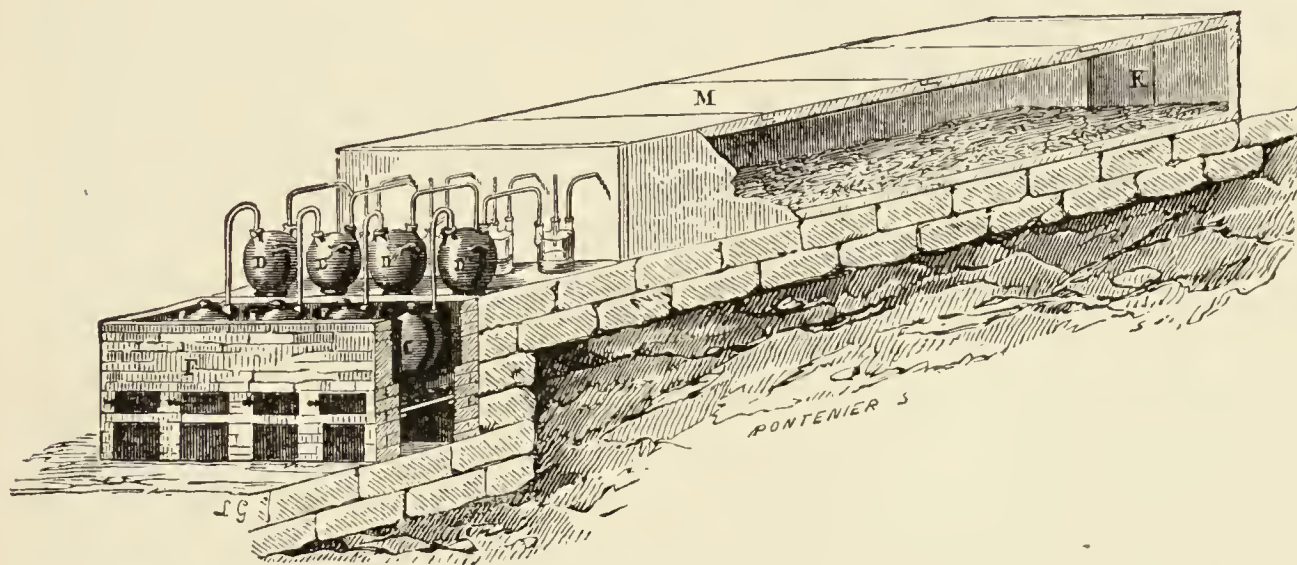


FIG. 77.—Apparatus for the manufacture of bleaching powder (on a small scale) by the action of chlorine, which is generated in the vessels C, on lime, which is charged into M.

$= 2\text{NaCl} + \text{HCl} + \text{Cl}_2 + \text{H}_2\text{O}$; (2) *oxygen*, as we saw in Chapter III. The bleaching properties and, in general, **oxidising action**, of bleaching salts are based on this evolution of oxygen (or chlorine); oxygen is also disengaged on heating the dry salts—for instance, $\text{NaCl} + \text{NaClO} = 2\text{NaCl} + \text{O}$; (3) and, lastly, *chlorine monoxide* which contains both chlorine and oxygen. Thus, if a little sulphuric, nitric, or similar acid (not enough to liberate hydrochloric acid from the CaCl_2) be added to a solution of a bleaching salt (which has an alkaline reaction, owing either to an excess of alkali or to the feeble acid properties of HClO), then the hypochlorous acid set free gives water and chlorine monoxide. If carbonic anhydride (or boracic or a similar very feeble acid) acts on the solution of a bleaching salt, hydrochloric acid is not evolved from the sodium or calcium chlorides, but the hypochlorous acid is displaced and gives chlorine

monoxide,³¹ because hypochlorous acid is one of the most feeble acids. Another method for the preparation of chlorine monoxide is based on these feeble acid properties of hypochlorous acid. Zinc oxide and mercury oxide, under the action of chlorine in the presence of water, do not give a salt of hypochlorous acid, but form a chloride and hypochlorous acid, which fact shows the incapacity of this acid to combine with the bases mentioned. Therefore, if such oxides as those of zinc or mercury be shaken up in water, and chlorine be passed through the turbid liquid,³² a reaction will occur which may be expressed in the following manner: $2\text{HgO} + 2\text{Cl}_2 = \text{Hg}_2\text{OCl}_2 + \text{Cl}_2\text{O}$. Here a compound of mercury oxide with mercury chloride, or the so-called mercury oxychloride, is obtained: $\text{Hg}_2\text{OCl}_2 = \text{HgO} + \text{HgCl}_2$. This is insoluble in water, and is not affected by hypochlorous anhydride, so that the solution will contain only hypochlorous acid, splitting up into the anhydride and water.^{32a}

Chlorine monoxide, which corresponds with bleaching and hypochlorous salts, containing as it does the two elements oxygen and chlorine, forms a characteristic example of a compound of elements which, in the majority of cases, act chemically in an analogous manner. Chlorine monoxide, as prepared from an aqueous solution by the abstraction of water or by the action of dry chlorine on cooled mercuric oxide, is, at the ordinary temperature, a gas or vapour which condenses into a red liquid boiling at $+20^\circ$ and giving a vapour whose

³¹ For this reason it is necessary that in the preparation of bleaching powder the chlorine should be free from hydrochloric acid, and even the lime from calcium chloride. An excess of chlorine, in acting on a solution of bleaching powder, may also give chlorine monoxide, because calcium carbonate also gives chlorine monoxide under the action of chlorine. This reaction may be brought about by treating freshly precipitated calcium carbonate in water with a stream of chlorine: $2\text{Cl}_2 + \text{CaCO}_3 = \text{CO}_2 + \text{CaCl}_2 + \text{Cl}_2\text{O}$. From this we may conclude that, although carbonic anhydride displaces hypochlorous anhydride, it may be itself displaced by an excess of the latter.

³² Red mercuric oxide acts on chlorine, forming dry hypochlorous anhydride (chlorine monoxide) (Balard); when mixed with water, red mercuric oxide acts feebly on chlorine, and when freshly precipitated it evolves oxygen and chlorine. An oxide of mercury which easily and abundantly evolves chlorine monoxide under the action of chlorine in the presence of water may be prepared as follows: the oxide of mercury, precipitated from a mercuric salt by an alkali, is heated to 300° and cooled (Pelouze). If a salt, MClO , be added to a solution of mercuric salt, HgX_2 , mercuric oxide is liberated, because the hypochlorite is decomposed.

^{32a} A solution of hypochlorous anhydride is also obtained by the action of chlorine on many salts; for example, in the action of chlorine on a solution of sodium sulphate the following reaction takes place: $\text{Na}_2\text{SO}_4 + \text{H}_2\text{O} + \text{Cl}_2 = \text{NaCl} + \text{HClO} + \text{NaHSO}_4$. Here the hypochlorous acid is formed, together with HCl , at the expense of the chlorine and water, for $\text{Cl}_2 + \text{H}_2\text{O} = \text{HCl} + \text{HClO}$. A dilute solution of hypochlorous acid or chlorine monoxide may be concentrated by distillation, and if a substance which takes up water (without destroying the acid)—for instance, calcium nitrate—be added to the stronger solution, then the anhydride of hypochlorous acid—i.e., chlorine monoxide—will be disengaged.

density (43 referred to hydrogen) shows that 2 vols. of chlorine and 1 vol. of oxygen give 2 vols. of chlorine monoxide. In an anhydrous form the gas or liquid **easily explodes**, splitting up into chlorine and oxygen. This explosiveness is determined by the fact that heat is evolved *in the decomposition* to the amount of about 15,000 heat units for Cl_2O .³³ The explosion may even take place spontaneously, and also in the presence of many oxidisable substances (for instance, sulphur, organic compounds, &c.); but the solution, although unstable and showing a strong oxidising tendency, does not explode.³⁴ It is evident that the presence of hypochlorous acid, HClO , may be assumed in an aqueous solution of Cl_2O , since $\text{Cl}_2\text{O} + \text{H}_2\text{O} = 2\text{HClO}$.

Hypochlorous acid, its salts, and chlorine monoxide serve as a transition between hydrochloric acid, chlorides, and chlorine, and a whole series of compounds containing the same elements combined with a still greater proportion of oxygen. The higher oxides of chlorine, as their origin indicates, are closely related to hypochlorous acid and its salts:

Cl_2 ,	NaCl ,	HCl ,	hydrochloric acid.
Cl_2O ,	NaClO ,	HClO ,	hypochlorous acid.
Cl_2O_3 ,	NaClO_2 ,	HClO_2 ,	chlorous acid. ³⁵
Cl_2O_5 ,	NaClO_3 ,	HClO_3 ,	chloric acid.
Cl_2O_7 ,	NaClO_4 ,	HClO_4 ,	perchloric acid.

³³ All explosive substances are of this kind—ozone, hydrogen peroxide, chloride of nitrogen, nitro-compounds, &c. Hence they easily decompose. In a liquid state chlorine monoxide explodes even on contact with powdery substances, or when rapidly agitated—for instance, if a file be rasped over the vessel in which it is contained.

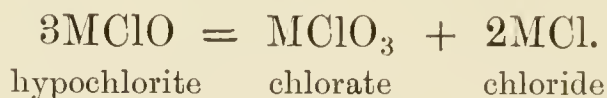
³⁴ A solution of chlorine monoxide, or hypochlorous acid, does not explode, owing to the presence of the mass of water. In dissolving, chlorine monoxide evolves about 9,000 heat units, so that its store of heat becomes less.

The capacity of hypochlorous acid (Carius and others) for entering into combination with the unsaturated hydrocarbons is very often taken advantage of in organic chemistry. Thus its solution absorbs ethylene, forming the chlorhydrin $\text{C}_2\text{H}_4\text{ClOH}$.

The oxidising action of hypochlorous acid and its salts is applied not only to bleaching, but also to many reactions of oxidation. Thus it converts the lower oxides of manganese into the peroxide.

³⁵ **Chlorous acid**, HClO_2 (according to the data given by Millon, Brandau, and others), in many respects resembles hypochlorous acid, HClO , whilst they both differ from chloric and perchloric acids in their degree of stability, evidenced, for instance, in their bleaching properties; the two higher acids do not bleach, but both the lower ones do so (oxidise at the ordinary temperature). On the other hand chlorous acid is analogous to nitrous acid, HNO_2 . The anhydride of chlorous acid, Cl_2O_3 , is not known in a pure state, but it probably occurs in admixture with the chlorine dioxide, ClO_2 , obtained by the action of nitric and sulphuric acids on a mixture of potassium chlorate with such reducing substances as nitric oxide, arsenious oxide, sugar, &c. Pure chlorine dioxide, ClO_2 (see notes 39–43) is gradually converted into a mixture of hypochlorous and chlorous acids under the action of water (and alkalies); that is, it acts like nitric peroxide, NO_2 (giving HNO_3 and HNO_2), or as a mixed anhydride, $2\text{ClO}_2 + \text{H}_2\text{O} = \text{HClO}_3 + \text{HClO}_2$. The silver salt, AgClO_2 , is sparingly soluble in water. The investigations of Garzarolli-Thurnlackh and others seem to show that the anhydride Cl_2O_3 does not exist in a free state.

When heated, solutions of hypochlorites undergo a remarkable change. Themselves so unstable, they, without any further addition, yield two fresh salts which are both much more stable; one contains more oxygen than MClO , the other contains none at all.



Part of the salt—namely, two-thirds of it—parts with its oxygen in order to oxidise the remaining third.³⁶ From an intermediate substance, two extremes are formed, just as nitrous anhydride splits up into nitric oxide and nitric anhydride (or nitric acid). The resulting salt, MClO_3 , corresponds with **chloric acid** and potassium chlorate, KClO_3 . It is evident that a similar salt may be obtained directly by the action of chlorine on an alkali if its solution be heated, because RClO will be first formed, and then RClO_3 ; for example, $6\text{KHO} + 3\text{Cl}_2 = \text{KClO}_3 + 5\text{KCl} + 3\text{H}_2\text{O}$. Chlorates are so prepared, for instance, **potassium chlorate**, which is easily separated from potassium chloride, being sparingly soluble in cold water.³⁷

³⁶ Hydrochloric acid, which is an example of compounds of this kind, is a saturated substance which does not combine directly with oxygen, but in which, nevertheless, a considerable quantity of oxygen may be inserted between the elements forming it. The same may be observed in a number of other cases. Thus oxygen may be added or inserted between the elements, sometimes in considerable quantities, in the saturated hydrocarbons; for instance, in C_3H_8 , three atoms of oxygen produce an alcohol, glycerin or glycerol, $\text{C}_3\text{H}_5(\text{OH})_3$. We shall meet with similar examples hereafter. This is generally explained by regarding oxygen as a bivalent element—that is, as capable of combining with two different elements, such as chlorine, hydrogen, &c. On the basis of this view, it may be inserted between each pair of combined elements; the oxygen will then be combined with one of the elements by one of its affinities and with the other element by its other affinity. This view does not, however, express the entire truth of the matter, even when applied to the compounds of chlorine. Hypochlorous acid, HOCl —that is, hydrochloric acid in which one atom of oxygen is inserted—is a substance of small stability; it might therefore be expected that on the addition of a fresh quantity of oxygen, a still less stable substance would be obtained, because, according to the above view, the chlorine and hydrogen, which form such a stable compound together, are then still further removed from each other. But it appears that chloric and perchloric acid, HClO_3 and HClO_4 , are much more stable substances. Furthermore, the addition of oxygen has also its limit; it can only be added to a certain extent. If the above representation were true and not merely hypothetical, there would be no limit to the combination of oxygen, and the more it entered into one continuous chain the more unstable would be the resultant compound. But not more than four atoms of oxygen can be added to hydrogen sulphide, or to hydrochloric acid, or to hydrogen phosphide. This peculiarity must lie in the properties of oxygen itself; four atoms of oxygen seem to have the power of forming a kind of radicle which retains two or several atoms of various other substances—for example, chlorine and hydrogen, hydrogen and sulphur, sodium and manganese, phosphorus and metals, &c., forming comparatively stable compounds, NaClO_4 , Na_2SO_4 , NaMnO_4 , Na_3PO_4 , &c. (see Chap. X., note 1, and Chap. XV.).

³⁷ If chlorine is passed through a *cold* solution of potash, a bleaching salt, potassium chloride and hypochlorite, $\text{KCl} + \text{KClO}$, is formed, but if it is passed through a *hot*

If dilute sulphuric acid is added to a solution of potassium chlorate, **chloric acid** is liberated, but it cannot be separated by distillation, as it is decomposed in the process. To obtain the free acid, sulphuric acid is added to a solution of barium chlorate.³⁸ The sulphuric acid

solution potassium chlorate is formed. As this is sparingly soluble in water, it chokes the gas-conducting tube, which should therefore be widened out at the end.

Potassium chlorate is usually obtained on a large scale from calcium chlorate, which is prepared by passing chlorine (as long as it is absorbed) into warm water containing lime. A mixture of calcium chlorate and chloride is thus formed in the solution. Potassium chloride is then added to the warm solution, and on cooling, a precipitate of potassium chlorate is formed as a substance which is sparingly soluble in cold water, especially in the presence of other salts. The double decomposition taking place is $\text{Ca}(\text{ClO}_3)_2 + 2\text{KCl} = \text{CaCl}_2 + 2\text{KClO}_3$. At the present time chlorate of potassium (and also KClO_4) is prepared exclusively by an electrolytic method. If a current is passed between platinum electrodes 10 mm. apart in a solution of KCl (1 part of salt to $2\frac{1}{2}$ parts of water) at 40° – 60° and containing some 1 per cent. of bichromate of potassium (this forms chromic oxide at the anode and counterbalances the reducing action of the hydrogen evolved at the cathode), the chlorine evolved at the anode (density of current should be 20 ampères per 100 sq. cm.) converts the caustic potash formed at the cathode into KClO_3 , which crystallises out as it accumulates, especially after cooling (Halenssermann and Naschold, 1894, and others). At lower temperatures KClO is formed. If the temperature of the solution is lowered, the KClO_3 gives KClO_4 under the action of the current. Both these salts are used in explosives, and are now exclusively prepared from KCl by these means.

Potassium chlorate readily crystallises in large colourless tabular crystals. Its solubility in 100 parts of water is 3 parts at 0° , 8 parts at 20° , 14 parts at 40° , 25 parts at 60° , and 40 parts at 80° . For comparison we will cite the following figures showing the solubility of potassium chloride and perchlorate in 100 parts of water: potassium chloride, 28 parts at 0° ; at 20° , 35 parts; at 40° , 40 parts; and at 100° , 57 parts; potassium perchlorate, at 0° , about 1 part; at 20° , about $1\frac{2}{3}$ part; and at 100° , about 18 parts. When heated, potassium chlorate melts (the melting-point has been given as from 335° to 376°) and decomposes with the evolution of oxygen, potassium perchlorate being at first formed, as will afterwards be described (see note 47). A mixture of potassium chlorate and nitric and hydrochloric acids effects oxidation and chlorination in solutions. It deflagrates when thrown upon incandescent carbon, and when mixed with sulphur ($\frac{1}{3}$ part by weight) it ignites it on being struck, in which case an explosion takes place. The same occurs with many metallic sulphides and organic substances. Such mixtures are also ignited by a drop of sulphuric acid. All these effects are due to the large amount of oxygen contained in potassium chlorate, and to the ease with which it is evolved. A mixture of two parts of potassium chlorate, one part of sugar, and one part of yellow prussiate of potash acts like gunpowder, but burns too rapidly, and therefore bursts the guns, and has also a very strong oxidising action on the metal. The sodium salt, NaClO_3 , is much more soluble than the potassium salt, and is therefore more difficult to free from sodium chloride, &c. The barium salt is also more soluble than the potassium salt: at 0° , 24 parts; at 20° , 37 parts; and at 80° , 98 parts of salt dissolve per 100 of water.

³⁸ Barium chlorate, $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$, is obtained by first preparing impure chloric acid and saturating it with baryta, the barium salt being purified by crystallisation. The impure free chloric acid is obtained by converting the potassium in potassium chlorate into an insoluble salt. This is done by adding tartaric or hydrofluosilicic acid to a solution of potassium chlorate, because potassium tartrate and potassium silicofluoride are very sparingly soluble in water. Chloric acid is readily soluble in water. The salts of Mg, Zn, Co, and Ni crystallise with 6 molecules of water, but above 15° – 30° they pass into $\text{R}(\text{ClO}_3)_2 \cdot 4\text{H}_2\text{O}$. Further heating gives a compound with $2\text{H}_2\text{O}$, which is

gives a precipitate of barium sulphate, and free chloric acid remains in solution. The solution may be evaporated under the receiver of an air-pump. This solution is colourless, has no smell, and acts as a powerful acid (it neutralises sodium hydroxide, decomposes sodium carbonate, gives hydrogen with zinc, &c.); when heated above 40° it decomposes, forming chlorine, oxygen, and perchloric acid: $4\text{HClO}_3 = 2\text{HClO}_4 + \text{H}_2\text{O} + \text{Cl}_2 + \text{O}_3$. In a concentrated condition the acid acts as an exceedingly energetic oxidiser, so that organic substances brought into contact with it burst into flame. Iodine, sulphurous acid, and similar oxidisable substances form higher oxidation products and reduce the chloric acid to hydrochloric acid. Hydrochloric acid gas gives chlorine with chloric acid (and consequently with KClO_3 also), acting in the same manner as it acts on the lower acids: $\text{HClO}_3 + 5\text{HCl} = 3\text{H}_2\text{O} + 3\text{Cl}_2$.

By cautiously acting on potassium chlorate with sulphuric acid, the **dioxide (chloric peroxide)**, ClO_2 ,³⁹ is obtained (Davy, Millon). This gas is easily liquefied in a freezing mixture, and boils at $+10^{\circ}$. The vapour density (about 35, taking H as 1) shows that the molecule of this substance is ClO_2 .⁴⁰ In a gaseous or liquid state it very easily explodes (for instance, at 60° , or by contact with organic compounds or finely divided substances, &c.), forming Cl and O_2 , and in many instances⁴¹ therefore it acts as an oxidising agent, although (like nitric peroxide) it may itself be further oxidised.⁴² In dissolving in water or alkalies,

also contained in the stable $\text{Cd}(\text{ClO}_3)_2 \cdot 2\text{H}_2\text{O}$. Thus in this case the amount of water of crystallisation varies by $2\text{H}_2\text{O}$, while with the nitrates it varies by $3\text{H}_2\text{O}$. The nitrates of the above metals are also less soluble than the chlorates (Meusser, 1902).

³⁹ To prepare ClO_2 , 100 grams of sulphuric acid are cooled in a mixture of ice and salt, and 15 grams of powdered potassium chlorate gradually added to the acid, which is then carefully distilled at 20° to 40° , the vapour given off being condensed in a freezing mixture: $3\text{KClO}_3 + 2\text{H}_2\text{SO}_4 = 2\text{KHSO}_4 + \text{KClO}_4 + 2\text{ClO}_2 + \text{H}_2\text{O}$. The reaction may result in an explosion. Calvert and Davies obtained chlorine peroxide without the least danger by heating a mixture of oxalic acid and potassium chlorate in a test-tube in a water-bath: $2\text{KClO}_3 + 3\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O} = 2\text{C}_2\text{HKO}_4 + 2\text{CO}_2 + 2\text{ClO}_2 + 8\text{H}_2\text{O}$. The reaction is still further facilitated by the addition of a small quantity of sulphuric acid.

⁴⁰ By analogy with nitrogen peroxide it might be expected that at low temperatures a doubling of the molecule into Cl_2O_4 would take place, as the reactions of ClO_2 point to its being a mixed anhydride of HClO_2 and HClO_3 .

⁴¹ Owing to the formation of this chlorine dioxide, a mixture of potassium chlorate and sugar is ignited by a drop of sulphuric acid. This property was formerly made use of for making matches, and is now sometimes employed for setting fire to explosive charges by means of an arrangement in which the acid is caused to fall on the mixture at the moment required. An interesting experiment on the combustion of phosphorus under water may be conducted with chlorine dioxide. Pieces of phosphorus and of potassium chlorate are placed under water, and sulphuric acid is poured on to them (through a long funnel); the phosphorus then burns at the expense of the chlorine dioxide.

⁴² Potassium permanganate oxidises chlorine dioxide into chloric acid (Fürst).

chlorine peroxide gives chlorous and hypochlorous acids— $2\text{ClO}_2 + 2\text{KHO} = \text{KClO}_3 + \text{KClO}_2 + \text{H}_2\text{O}$ —and therefore, like nitric peroxide, the dioxide may be regarded as an intermediate oxide between the (unknown) anhydrides of chlorous and chloric acids : $4\text{ClO}_2 = \text{Cl}_2\text{O}_3 + \text{Cl}_2\text{O}_5$.⁴³

As the salts of chloric acid, HClO_3 , are produced by the splitting up of those of hypochlorous acid, so in the same way the salts of perchloric acid, HClO_4 , are produced from the salts of chloric acid, HClO_3 . But this is the highest form of the oxidation of HCl . **Perchloric acid**, HClO_4 , in a free state, is the most stable of all the acids of chlorine. When fused potassium chlorate begins to swell up and solidify, after having parted with one-third of its oxygen, potassium chloride and potassium perchlorate have been formed according to the equation : $2\text{KClO}_3 = \text{KClO}_4 + \text{KCl} + \text{O}_2$.

The formation of this salt is easily observed in the preparation of oxygen from potassium chlorate, owing to the fact that the potassium perchlorate fuses with greater difficulty than the chlorate, and therefore appears in the molten salt as solid grains (see Chap. III., note 12). Under the action of an electric current and of certain acids—for instance, sulphuric and nitric—potassium chlorate also gives potassium perchlorate. This latter may be easily purified, because it is but sparingly soluble in water, although other salts of perchloric acid are very soluble and even deliquesce in the air. The perchlorates, although they contain more oxygen than the chlorates, are decomposed with greater difficulty, and even when thrown on ignited charcoal give a much feebler deflagration than the chlorates. Sulphuric acid on heating causes the evolution of volatile and to a certain extent stable perchloric acid from potassium perchlorate. Perchloric acid can be distilled.⁴⁴ The pure hydrate HClO_4 ⁴⁵ is a colourless and exceedingly caustic

⁴³ The euchlorine obtained by Davy by gently heating potassium chlorate with hydrochloric acid is (Pebal) a mixture of chlorine dioxide and free chlorine.

⁴⁴ If a solution of chloric acid, HClO_3 , be first concentrated over sulphuric acid under the receiver of an air-pump and afterwards distilled, chlorine and oxygen are evolved and perchloric acid formed : $4\text{HClO}_3 = 2\text{HClO}_4 + \text{Cl}_2 + 3\text{O} + \text{H}_2\text{O}$. Roscoe accordingly decomposed a solution of potassium chlorate directly by hydrofluosilicic acid, decanted it from the precipitate of potassium silicofluoride, K_2SiF_6 , concentrated the solution of chloric acid, and then distilled it, perchloric acid being then obtained (see following footnote). That chloric acid is capable of passing into perchloric acid is also seen from the fact that potassium permanganate is decolorised, although slowly, by the action of a solution of chloric acid. Perchloric acid is also formed by the action of an electric current on solutions of chlorine and chlorine monoxide. Perchloric acid was obtained by Count Stadion and afterwards by Serullas, and was studied by Roscoe and others.

⁴⁵ Perchloric acid, being volatile, is partially decomposed by distillation. The solution obtained after distillation may be concentrated by evaporation in open vessels. In the distillation the solution reaches a temperature of 200° , and a very constant liquid hydrate of the composition $\text{HClO}_4 \cdot 2\text{H}_2\text{O}$ is then obtained in the distillate. If this hydrate is mixed with sulphuric acid, it begins to decompose at 100° , but nevertheless a portion of

substance which fumes in the air and has a specific gravity 1.78 at 15° (sometimes, after being kept for some time, it decomposes with a violent explosion). It explodes violently when brought into contact with charcoal, paper, wood, and other organic substances. If a small quantity of water be added to this hydrate, and it be cooled, a crystallo-hydrate, $\text{ClHO}_4 \cdot \text{H}_2\text{O}$, separates out. This is much more stable, but the liquid hydrate, $\text{HClO}_4 \cdot 2\text{H}_2\text{O}$, is still more so. The acid dissolves in water in all proportions, and its solutions are distinguished for their stability.⁴⁶ When ignited, both the acid and its salts are decomposed, with the evolution of oxygen.⁴⁷

the acid passes over into the receiver without decomposing, forming a crystalline hydrate, $\text{HClO}_4 \cdot \text{H}_2\text{O}$, which melts at 50°. On carefully heating this hydrate it breaks up into perchloric acid, which distils over below 100°, and into the liquid hydrate, $\text{HClO}_4 \cdot 2\text{H}_2\text{O}$. The acid HClO_4 may also be obtained by adding one-fourth part of strong sulphuric acid to potassium chlorate, carefully distilling and subjecting the crystals of the hydrate, $\text{HClO}_4 \cdot \text{H}_2\text{O}$, obtained in the distillate, to a fresh distillation. Perchloric acid, HClO_4 , itself does not distil, and is decomposed on distillation until the more stable hydrate, $\text{HClO}_4 \cdot \text{H}_2\text{O}$, is formed; this decomposes into HClO_4 and $\text{HClO}_4 \cdot 2\text{H}_2\text{O}$, which latter hydrate distils without decomposition. This forms an excellent example of the influence of water on stability, and shows the property of chlorine of giving compounds of the type ClX_7 , of which all the above hydrates, $\text{ClO}_3(\text{OH})$, $\text{ClO}_2(\text{OH})_3$, and $\text{ClO}(\text{OH})_5$, are members. Probably further research will lead to the discovery of a hydrate $\text{Cl}(\text{OH})_7$.

⁴⁶ According to Roscoe the specific gravity of perchloric acid is 1.782 and that of the hydrate $\text{HClO}_4 \cdot \text{H}_2\text{O}$ in a liquid state (50°), 1.811; hence a considerable contraction takes place in the combination of HClO_4 with H_2O .

⁴⁷ The decomposition of salts analogous to potassium chlorate has been more fully studied by Potilitzin and P. Frankland. Professor Potilitzin, by decomposing, for example, lithium chlorate LiClO_3 , found (from the quantities of lithium chloride and oxygen) that at first the decomposition of the fused salt (368°) takes place according to the equation, $3\text{LiClO}_3 = 2\text{LiCl} + \text{LiClO}_4 + 5\text{O}$, and that towards the end the remaining salt is decomposed thus: $5\text{LiClO}_3 = 4\text{LiCl} + \text{LiClO}_4 + 10\text{O}$. The phenomena observed by Potilitzin obliged him to admit that lithium perchlorate is capable of decomposing simultaneously with lithium chlorate, with the formation of the latter salt and oxygen; and this was confirmed by direct experiment, which showed that lithium chlorate is always formed in the decomposition of the perchlorate. Potilitzin drew particular attention to the fact that the decomposition of potassium chlorate and of salts analogous to it, although these are exothermal (Chap. III., note 12) not only does not proceed spontaneously, but requires time and a rise of temperature in order to attain completion, which again shows that chemical equilibria are not determined by the heat effects of reactions only.

P. Frankland and J. Dingwall (1887) showed that at 448° (in the vapour of sulphur) a mixture of potassium chlorate and powdered glass is decomposed almost in accordance with the equation, $2\text{KClO}_3 = \text{KClO}_4 + \text{KCl} + \text{O}_2$, whilst the salt by itself evolves about half as much oxygen, according to the equation, $8\text{KClO}_3 = 5\text{KClO}_4 + 3\text{KCl} + 2\text{O}_2$. The decomposition of potassium perchlorate in admixture with manganese peroxide proceeds to completion, $\text{KClO}_4 = \text{KCl} + 2\text{O}_2$. But in decomposing by itself the salt at first gives potassium chlorate, approximately according to the equation, $7\text{KClO}_4 = 2\text{KClO}_3 + 5\text{KCl} + 11\text{O}_2$. Thus there is now no doubt that when potassium chlorate is heated, the perchlorate is formed, and that this salt, in decomposing with evolution of oxygen, again gives the former salt.

In the decomposition of barium hypochlorite, 50 per cent. of the whole amount passes

On comparing chlorine as an element not only with nitrogen and carbon but with all the other non-metallic elements, we find in it the following fundamental **properties of the halogens** or salt-producers. With metals, chlorine gives salts (such as sodium chloride, &c.), and with hydrogen, a very energetic and monobasic acid HCl, and the same quantity of chlorine is able by metalepsis to replace the hydrogen; with oxygen it forms unstable oxides of an acid character. These properties are possessed by three other elements, bromine, iodine, and fluorine. These are all members of one natural family. Each representative has its peculiarities, its individual properties and points of distinction, in combination and in the free state—otherwise they would not be independent elements; but the repetition in all of them of the same chief characteristics of the family enables one more quickly to grasp all their various properties and facilitates our acquaintance with them.

In order to have a guiding thread in forming comparisons between the elements, attention must, however, be turned not only to their points of resemblance, but also to those in which they differ most from each other. And the **atomic weights** of the elements must be considered as their most elementary property, since this is a quantity which is most firmly established, and must be taken account of in all the reactions of the element. The halogens have the following atomic weights—

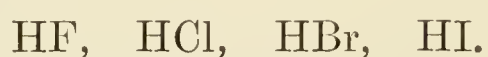
$$\text{F}=19, \quad \text{Cl}=35.5, \quad \text{Br}=80, \quad \text{I}=127.$$

All the properties, physical and chemical, of the elements and their corresponding compounds must evidently be in a certain dependence on this fundamental point, if the grouping in one family be natural. And we find in reality that, for instance, the properties of bromine, whose atomic weight is almost the mean between those of iodine and chlorine, occupy a mean position between those of these two elements.

into chlorate, in that of strontium hypochlorite (Potilitzin, 1890) 12.5 per cent., and with calcium hypochlorite about 2.5 per cent. Besides which, Potilitzin showed that the decomposition of the hypochlorites and also of the chlorates is always accompanied by the formation of a certain quantity of the oxides and by the evolution of chlorine, the chlorine being displaced by the oxygen disengaged.

The decomposition of potassium chlorate, being a reaction evolving heat, easily lends itself, for this reason, to the contact action of manganese peroxide and other similar admixtures; for such very feeble influences as those of contact may become evident either in those cases (for instance, detonating gas, hydrogen peroxide, &c.), when the reaction is accompanied by the evolution of heat, or when (for instance, $\text{H}_2 + \text{I}_2$, &c.) little heat is absorbed or evolved. In these cases it is evident that the existing equilibrium is not very stable, and that a small alteration in the conditions at the surfaces of contact may suffice to upset it. In order to conceive the *modus operandi* of contact phenomena, it is enough to imagine, for instance, that at the surface of contact the movement of the atoms in the molecules changes from a circular to an elliptical path.

The second measurable property of the elements is their equivalence or their capacity for forming **compounds of definite forms**. Thus carbon or nitrogen in this respect differs widely from the halogens. Although the form ClO_2 corresponds with NO_2 and CO_2 , yet the last is the highest oxide of carbon, whilst that of nitrogen is N_2O_5 , and for chlorine, if there were an anhydride of perchloric acid, its composition would be Cl_2O_7 , which is quite different from that of carbon. In respect to the form of their compounds the halogens, like all elements of one family or group, are perfectly analogous with each other, as is seen from their hydrogen compounds :



Their oxygen compounds exhibit a similar analogy. Fluorine alone does not give any oxygen compounds. The iodine and bromine compounds corresponding with HClO_3 and HClO_4 are HBrO_3 and HBrO_4 , HIO_3 and HIO_4 . On comparing the properties of these acids, we can even predict that fluorine will not form any oxygen compound. For iodine is easily oxidised—for instance, by nitric acid—whilst chlorine is not directly oxidised. The oxygen acids of iodine are comparatively more stable than those of chlorine; and, generally speaking, the affinity of iodine for oxygen is much greater than that of chlorine. Here also bromine occupies an intermediate position. In fluorine we may therefore expect a still smaller affinity for oxygen than in chlorine—and up to now it has not been combined with oxygen. If any oxygen compounds of fluorine should be obtained, they will naturally be exceedingly unstable. The relation of these elements to hydrogen is the reverse of the above. Fluorine has so great an affinity for hydrogen that it decomposes water at the ordinary temperature; whilst iodine has so little affinity for hydrogen that hydriodic acid, HI , is formed with difficulty, is easily decomposed, and frequently acts as a reducing agent.

From the form of their compounds the halogens are **univalent elements** with respect to hydrogen and septivalent with respect to oxygen, N being trivalent to hydrogen (it gives NH_3) and quinquevalent to oxygen (it gives N_2O_5), and C quadrivalent to both H and O, as it forms CH_4 and CO_2 . And as not only their oxygen compounds, but also their hydrogen compounds, have acid properties, the halogens are **elements of an exclusively acid character**. In no other elements is the acid-giving property so strongly developed as in the halogens.^{47a}

^{47a} Among the general properties of the haloids must be mentioned the faculty for a mutual union between the metallic and metalloidal compounds formed by them, or the formation of complex haloid salts like the oxygen salts, where MX_n (M a metal, X a haloid) combines with RX_n (R either a metal or metalloid) to form $\text{MRX}_{(n+m)}$ or some

In describing certain peculiarities characterising the halogens, we shall at every step encounter a confirmation of the above-mentioned general relations.

As **fluorine** decomposes water with the evolution of oxygen, in the form of ozone, $F_2 + H_2O = 2HF + O$, for a long time all efforts to obtain it in the free state by means of methods similar to those used for the preparation of chlorine proved fruitless.⁴⁸ Thus by the action of hydrofluoric acid on manganese peroxide, or by decomposing a solution of hydrofluoric acid by an electric current, either oxygen or a mixture of oxygen and fluorine was obtained instead of fluorine. Probably a certain quantity of fluorine^{48a} was set free by the action of oxygen or an electric current on incandescent and fused calcium fluoride, but at a high temperature fluorine acts even on platinum, and therefore it was not isolated. When chlorine acted on silver fluoride, AgF , in a vessel of natural fluor spar, CaF_2 , fluorine was also liberated; but it was mixed with chlorine, and it was impossible to study the properties of the resultant gas. Brauner (1881) also obtained fluorine by igniting cerium fluoride, $2CeF_4 = 2CeF_3 + F_2$; but this, like all preceding efforts, only showed fluorine to be a gas which decomposes water and is capable of acting in a number of instances like chlorine, but gave no possibility of testing its properties. It was evident that it was necessary to avoid as far as possible the presence of water and a rise of temperature; this Moissan succeeded in doing in 1886. He decomposed anhydrous hydrofluoric acid (to which a small quantity of potassium fluoride had been added to make it a better conductor), liquefied at a temperature of -23° and contained in a platinum or copper U-shaped tube, by the action of a powerful electric current (twenty Bunsen's elements in series). Hydrogen was then evolved at the negative pole, and fluorine appeared at the positive pole (of iridium-platinum) as a pale green gas which

other simple multiple of them. Here M may be hydrogen and then the corresponding acid will be formed; for instance, $H_2SiF_4 = 2HF + SiF_4$, $HCuCl_2 = HCl + CuCl$, $HPtCl_3 = HCl + PtCl_2$, $H_2PtCl_6 = 2HCl + PtCl_4$, $H_2SnBr_6 = 2HBr + SnBr_4$, $HTeI_5 = HI + TeI_4$; or with their corresponding salts, where H is replaced by a metal; for example, K_2SiF_6 , K_2HgCl_4 , $(NH_4)_2PtCl_6$, H_2FeCl_6 , &c. The molecules of such double salts usually, as Werner remarked, contain—in the limit—six atoms of the haloid (see also Chap. XIII., note 3a, formation of KCl_4I).

⁴⁸ Even before free fluorine was obtained (1886) it was evident from experience gained in the efforts made to obtain it, and from analogy, that it would decompose water.

^{48a} It is most likely that in this experiment of Fremy's, which corresponds with the action of oxygen on calcium chloride, fluorine was set free, but that a converse reaction also proceeded, $CaO + F_2 = CaF_2 + O$, that is, the calcium distributed itself between the oxygen and fluorine. MnF_4 , which is capable of splitting up into MnF_2 and F_2 , is formed by the action of a strong solution of hydrofluoric acid on manganese peroxide, but under the action of water the fluorine gives hydrofluoric acid, and probably this is aided by the affinity of the manganese fluoride and hydrofluoric acid.

decomposed water with the formation of ozone and hydrofluoric acid, and combined directly with silicon (forming silicon fluoride, SiF_4), boron (forming BF_3), sulphur, &c. Its density shows that its molecule is F_2 . Fluorine liquefies under great cold into a yellow mobile liquid, boiling at -187° and solidifying at -210° . Liquid fluorine mixes with liquid air. Its density is 1.14, and it does not act upon glass, ice, or water, but it immediately bursts into flame with hydrogen or hydrocarbons (Moissan and Dewar, 1897). But the action of fluorine on metals at the ordinary temperature is comparatively feeble, because the metallic fluoride formed coats the remaining mass of the metals; however, Na, Fe, and others burn in fluorine. Hydrocarbons (such as naphtha), alcohol, &c., are immediately decomposed by fluorine, with the formation of hydrofluoric acid. Fluorine with hydrogen explodes violently, forming hydrofluoric acid;⁴⁹ even HCl is decomposed by fluorine, forming HF and Cl.

In 1894 Brauner obtained fluorine directly by igniting the easily formed^{49a} double lead salt, $\text{HF}, 3\text{KF}, \text{PbF}_4$, which first, at 230° , decomposes with the evolution of HF, and then splits up, forming $3\text{KF}, \text{PbF}_2$ and fluorine, F_2 , which is recognised by the fact that it liberates iodine from KI and easily combines with silicon, forming SiF_4 . Here, as a matter of fact, the higher degree of combination, PbF_4 , decomposes into

⁴⁹ According to Moissan, fluorine is disengaged by the action of an electric current on fused hydrogen potassium fluoride, KHF_2 . The present state of chemical knowledge is such that the knowledge of the properties of an element is much more general than the knowledge of the free element itself. It is useful and satisfactory to learn that even fluorine in the free state has not succeeded in eluding experiment and research, that the efforts to isolate it have been crowned with success, but the sum total of chemical data concerning fluorine as an element gains but little by this achievement. We may add that Moissan (1892) found that free fluorine decomposes H_2S , HCl, HBr, CS_2 , and CNH with a flash; it does not act upon O_2 , N_2 , CO, and CO_2 ; Mg, Al, Ag, and Ni, when heated, burn in it, as also do S, Se, P (forms PF_3); it reacts upon H_2 even in the dark, with the evolution of 36,600 units of heat. Soot and carbon in general (but not the diamond), when heated in gaseous fluorine, forms **fluoride of carbon**, CF_4 (Moissan, 1890); this compound is also formed at 300° by the double decomposition of CCl_4 and AgF ; it is a gas which liquefies at 10° under a pressure of five atmospheres. With an alcoholic solution of KHO, CF_4 gives K_2CO_3 , according to the equation, $\text{CF}_4 + 6\text{KHO} = \text{K}_2\text{CO}_3 + 4\text{KF} + 3\text{H}_2\text{O}$. CF_4 is not soluble in water, but is readily soluble in CCl_4 and alcohol. In 1900 Moissan and Lebeau showed that fluorine in combining with sulphur forms *hexafluoride of sulphur*, SF_6 , in the form of an inactive gas (see Chap. XX.).

^{49a} T. Nikolukin (1885), Classen, and others obtained PbCl_4 and a double ammonium salt of tetrachloride of lead (starting from the binoxide), $\text{PbCl}_4, 2\text{NH}_4\text{Cl}$; Hutchinson and Pallard obtained a similar salt of acetic acid (1893), corresponding to PbX_4 , by treating red lead with strong acetic acid; the composition of this salt is $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_4$ and it melts (and decomposes) at about 175° . Brauner (1894) obtained tetrafluoride of lead, PbF_4 , and the corresponding acid H_4PbF_8 . For example, by treating potassium plumbate (Chap. XVIII., note 55) with strong HF, and also the above-mentioned tetra-acetate with a solution of KHF_2 , Brauner obtained crystalline HK_3PbF_8 , which is the salt from which he obtained fluorine.

the lower, PbF_2 , and fluorine just as Cu_2Cl_2 decomposes into Cu_2Cl and chlorine.

Among the compounds of fluorine, calcium fluoride, CaF_2 , is somewhat widely distributed in nature as **fluor spar**,⁵⁰ whilst **cryolite**, or aluminium sodium fluoride, Na_3AlF_6 , is found more rarely (in large masses in Greenland). Cryolite, like fluor spar, is insoluble in water, and gives hydrofluoric acid with sulphuric acid. Small quantities of fluorine have also in a number of cases been found in the bodies of animals, in the blood, urine, and bones. If fluorides occur in the bodies of animals, they must have been introduced in food, and must occur in plants and in water. And as a matter of fact, river, and especially sea, water always contains a certain, although small, quantity of fluorine compounds.

Hydrofluoric acid, HF, cannot be obtained from fluor spar in glass retorts, because glass is acted on by, and destroys, the acid. It is prepared in lead, or, when it is required pure, in platinum vessels, because although lead acts on hydrofluoric acid, it does so only very feebly on the surface, and when once a coating of fluoride and sulphate of lead is formed no further action takes place. Powdered fluor spar and sulphuric acid evolve hydrofluoric acid (which fumes in the air) even at the ordinary temperature, $\text{CaF}_2 + \text{H}_2\text{SO}_4 = \text{CaSO}_4 + 2\text{HF}$. At 130° fluor spar is completely decomposed by sulphuric acid. The acid is then evolved as vapour, which may be condensed by a freezing mixture into an anhydrous acid. The condensation is aided by pouring water into the receiver of the condenser, as the acid is readily soluble in water.

In the liquid anhydrous form hydrofluoric acid boils at $+19^\circ$, and its specific gravity at 12.8° is 0.9849.⁵¹ It dissolves in water with the

⁵⁰ It is called spar because it occurs as crystals of a clearly laminar structure, and is therefore easily split up into pieces bounded by planes. It is called fluor spar because when used as a flux it renders ores fusible, owing to its reacting with silica, $\text{SiO}_2 + 2\text{CaF}_2 = 2\text{CaO} + \text{SiF}_4$; the silicon fluoride escapes as a gas and the lime combines with a further quantity of silica, giving a vitreous slag. Fluor spar occurs in mineral veins and rocks, sometimes in considerable quantities. It always crystallises in the cubic system, sometimes in very large semi-transparent cubic crystals, which are either colourless or of different colours. It is insoluble in water. It melts under the action of heat and crystallises on cooling. The specific gravity is 3.1. When steam is passed over incandescent fluor spar, lime and hydrofluoric acid are formed: $\text{CaF}_2 + \text{H}_2\text{O} = \text{CaO} + 2\text{HF}$. A double decomposition is also easily produced by fusing fluor spar with sodium or potassium hydroxide, or even with their carbonates; the fluorine then passes over to the potassium or sodium, and the oxygen to the calcium. Potassium fluoride is soluble in water, and precipitates CaF_2 from solutions of salts of calcium; for instance, $\text{Ca}(\text{NO}_3)_2 + 2\text{KF} = \text{CaF}_2 \text{ (precipitate)} + 2\text{KNO}_3$. Twenty-six thousand parts of water dissolve one part of fluor spar.

⁵¹ According to Gore. Fremy obtained anhydrous hydrofluoric acid by decomposing lead fluoride at a red heat by means of hydrogen, or by heating the double salt HKF_2 , which crystallises easily (in cubes) from a solution of hydrofluoric acid half of which has been saturated with potassium hydroxide.

evolution of a considerable amount of heat, and gives a solution of constant boiling-point which distils over at 120° , showing that the acid is able to combine with water. The specific gravity of the compound is 1.15, and its composition $\text{HF}, 2\text{H}_2\text{O}$.⁵² With an excess of water a dilute solution distils over first. Strong solutions and the acid itself must be kept in platinum vessels, but the dilute acid may be conveniently preserved in vessels made of gutta-percha, or even in glass vessels having an interior coating of paraffin. Hydrofluoric acid does not act on hydrocarbons and many other substances, but it acts in a highly corrosive manner on metals, glass, porcelain, and the majority of rock substances.⁵³ It also attacks the skin, and is distinguished by its very poisonous properties, so that in working with the acid a strong draught must be kept up, to prevent the possibility of the fumes being inhaled. The non-metals do not act on hydrofluoric acid, but all metals—with the exception of mercury, silver, gold, and platinum, and, to a certain degree, lead—decompose it with the evolution of hydrogen. With bases it gives directly metallic fluorides, and behaves in many respects like hydrochloric acid. There are, however, several distinct individual differences, which are furthermore much greater than those between hydrochloric, hydrobromic, and hydriodic acids. Thus the silver compounds of the latter are insoluble in water, whilst silver fluoride, AgF , is soluble. Calcium fluoride, on the contrary, is insoluble in water, whilst calcium chloride, bromide, and iodide are not only soluble,

⁵² All the properties of hydrofluoric acid recall those of hydrochloric acid, and the comparative ease with which hydrofluoric acid is liquefied (it boils at $+19^{\circ}$, hydrochloric acid at -83°) must therefore be explained by a polymerisation taking place at low temperatures, as will be afterwards explained, H_2F_2 being formed, and therefore in a liquid state it differs from hydrochloric acid, in which a phenomenon of a similar kind has not yet been observed. Solutions containing 70 per cent. of HF do not freeze at -70° , but at -45° a 58 per cent. solution forms a hydrate, $\text{HF}, \text{H}_2\text{O}$, which melts at -35° (Metzner, 1899).

⁵³ The corrosive action of hydrofluoric acid on glass and similar silicious compounds is based upon the fact that it acts on silica, SiO_2 , as we shall consider more fully in describing that compound (Chap. XVIII.), forming gaseous silicon fluoride, $\text{SiO}_2 + 4\text{HF} = \text{SiF}_4 + 2\text{H}_2\text{O}$. Silica, indeed, forms the binding (acid) element of glass and of the mass of mineral substances forming the salts of silica. When it is removed the cohesion is destroyed. This is made use of in the arts, and in the laboratory, for etching designs and scales, &c., on glass. In **engraving on glass** the surface is covered with a varnish composed of four parts of wax and one part of turpentine. This varnish is not acted on by hydrofluoric acid, and it is soft enough to allow of designs being drawn upon it whose lines lay bare the glass. The drawing is made with a steel point, and the glass is afterwards laid in a lead trough in which a mixture of fluor spar and sulphuric acid is placed. The sulphuric acid must be used in considerable excess, as otherwise transparent lines are obtained (owing to the formation of hydrofluosilicic acid). After being exposed for some time, the varnish is removed (melted) and the design drawn by the steel point is found reproduced in dull lines. The drawing may be also made by the direct application of a mixture of a silicofluoride and sulphuric acid, which forms hydrofluoric acid.

but attract water with great energy. Neither hydrochloric, nor hydrobromic, nor hydriodic acid acts on sand and glass, whilst hydrofluoric acid corrodes them, forming gaseous silicon fluoride, SiF_4 . The other halogen acids form normal salts, KCl , NaCl , with Na or K , whilst hydrofluoric acid gives acid salts—for instance, HKF_2 (and by dissolving KF in liquid HF , the compound $\text{KHF}_2 \cdot 2\text{HF}$ is obtained). This latter property is in close connection with the fact that at the ordinary temperature the vapour density of hydrofluoric acid is nearly 20, which corresponds with a formula H_2F_2 , as was shown by Mallet (1881); but a de-polymerisation occurs with a rise of temperature, and the density approaches 10, corresponding with the formula HF .⁵⁴

The analogy between chlorine and the other two halogens, bromine and iodine, is much more perfect. Not only have their hydrates or halogen acids much in common, but they themselves resemble chlorine in many respects,⁵⁵ and even the properties of the corresponding

⁵⁴ Mallet (1881) determined the density at 30° and 100° , previous to which Gore (1869) had determined the vapour density at 100° , whilst Thorpe and Hambly (1888) made fourteen determinations between 26° and 88° , and showed that within this limit of temperature, the density gradually diminishes, just as with the vapours of acetic acid, nitrogen dioxide, and others. The tendency of HF to polymerise into H_2F_2 is probably connected with the property of many fluorides of forming acid salts—for example, KHF_2 and H_2SiF_6 . We saw above that HCl has the same property (forming, for instance, H_2PtCl_6 , &c.), and hence this property of hydrofluoric acid does not stand isolated from the properties of the other halogens (see note 47a).

⁵⁵ For instance, the experiment with Dutch metal foil (note 16) may be made with bromine just as well as with chlorine. A very instructive experiment on the direct combination of the halogens with metals may be made by throwing a small piece (a shaving) of aluminium into a vessel containing liquid bromine; the aluminium, being lighter, floats on the bromine, and after a certain time reaction sets in accompanied by the evolution of heat, light, and fumes of bromine. The incandescent piece of metal moves rapidly over the surface of the bromine in which the resultant aluminium bromide dissolves. For the sake of comparison we shall proceed to give several thermochemical data (Thomson) for analogous actions of (1) chlorine, (2) bromine, and (3) iodine, with respect to metals, the halogen being expressed by the symbol X , and the plus sign connecting the reacting substances. All the figures are given in thousands of calories, and refer to molecular quantities in grams and to the ordinary temperature.

	1	2	3
$\text{K}_2 + \text{X}_2$	211	191	160
$\text{Na}_2 + \text{X}_2$	195	172	138
$\text{Ag}_2 + \text{X}_2$	59	45	28
$\text{Hg}_2 + \text{X}_2$	83	68	48
$\text{Hg} + \text{X}_2$	63	51	34
$\text{Ca} + \text{X}_2$	170	141	—
$\text{Ba} + \text{X}_2$	195	170	—
$\text{Zn} + \text{X}_2$	97	76	49
$\text{Pb} + \text{X}_2$	83	64	40
$\text{Al} + \text{X}_2$	161	120	70

In every case chlorine gives more heat than bromine, and bromine more than iodine.

metallic compounds of bromine and iodine are very much alike. Thus, the chlorides, bromides, and iodides of sodium and potassium crystallise in the cubic system, and are soluble in water; the chlorides of calcium, aluminium, magnesium, and barium are just as soluble in water as the bromides and iodides of these metals. The iodides and bromides of silver and lead are sparingly soluble in water, like the chlorides of these metals. The oxygen compounds of bromine and iodine also present a very strong analogy to the corresponding compounds of chlorine. A hypobromous acid is known corresponding with hypochlorous acid. The salts of this acid have the same bleaching property as the salts of hypochlorous acid. Iodine was discovered in 1811 by Courtois in kelp, and was shortly afterwards investigated by Clement, Gay-Lussac, and Davy. Bromine was discovered in 1826 by Balard in the mother liquor of sea water.

Bromine and iodine, like chlorine, occur in sea water in combination with metals. However, the amount of bromides, and especially of iodides, in sea water is so small that their presence can only be discovered by means of sensitive reactions.⁵⁶ In the extraction of salt from sea water the bromides remain in the mother liquor. Iodine and bromine also occur combined with silver, in admixture with silver chloride, as a rare ore found mainly in America. Certain mineral waters (those of Kreuznach and Staro-russki) contain metallic bromides and iodides, always in admixture with an excess of sodium chloride. Those upper strata of the Stassfurt rock salt (Chapter X.) which are a source of potassium salts also contain metallic bromides,⁵⁷ which collect in the mother liquors left after the crystallisation of the potassium salts; and this now forms the chief source (together with certain American springs) of the bromine in common use. Bromine may be easily liberated from a mixture of bromides and chlorides, owing to the fact that chlorine displaces bromine from its compounds with sodium, magnesium, calcium, &c. Colourless solutions of bromides of the

According to Esbreicher (1896), the following are the data for the liquefied halogen acids:—

	HCl	HBr	HI
Temperature of fusion	— 111.1°	— 87.9°	— 50.8°
Boiling-point	— 83.7°	— 64.9°	— 34.1°

We may remark that the latent heat of vaporisation of the molecular weight Br_2 is about 7.2, and that of iodine 6.0 thousand heat units, whilst the latent heat of fusion of Br_2 is about 0.3, and that of I_2 about 3.0 thousand heat units. From this it is evident that the difference between the amounts of heat evolved does not depend on the difference in physical state. For instance, the vapour of iodine in combining with Zn to form ZnI_2 would give $49 + 8 + 3$, or about sixty thousand heat units, or $1\frac{1}{2}$ time less than $\text{Zn} + \text{Cl}_2$

⁵⁶ One litre of sea water contains about 20 grams of chlorine, and about 0.07 gram of bromine. The Dead Sea contains about ten times as much bromine.

⁵⁷ But there is no iodine in Stassfurt carnallite.

metals turn an orange colour after the passage of chlorine, owing to the disengagement of bromine.⁵⁸ Bromine may be extracted on a large scale by a similar method, but it is simpler to add a small quantity of manganese peroxide and sulphuric acid to the mother liquid direct. This sets free a portion of the chlorine, and this chlorine liberates the bromine.

Bromine is a **dark brown liquid**, giving brown fumes, and having a poisonous suffocating smell, whence its name (from the Greek $\beta\rho\omega\mu\omicron\varsigma$, signifying evil-smelling). The vapour density of bromine shows that its molecule is Br_2 . In the cold, bromine freezes into brown-grey scales. The melting-point of pure bromine is -7.05° .⁵⁹ The density

⁵⁸ The chlorine must not, however, be in large excess, as otherwise the bromine would contain chlorine. Commercial bromine not infrequently contains chlorine, in the form of bromine chloride; this is more soluble in water than bromine, from which it may thus be freed. To obtain pure bromine the commercial product is washed with water, dried by means of sulphuric acid, and distilled, the portion coming over at 58° being collected; the greater part is then converted into potassium bromide and dissolved, and the remainder added to the solution in order to separate iodine, which is removed by shaking with carbon bisulphide. By heating the potassium bromide thus obtained with manganese peroxide and sulphuric acid, bromine is obtained quite free from iodine, which, however, is not present in certain kinds of commercial bromine (the Stassfurt, for instance). By treatment with potash, the bromine is then converted into a mixture of potassium bromide and bromate, and the mixture (which is in the proportion given in the equation) is distilled with sulphuric acid, bromine being then evolved: $5\text{KBr} + \text{KBrO}_3 + 6\text{H}_2\text{SO}_4 = 6\text{KHSO}_4 + 3\text{H}_2\text{O} + 3\text{Br}_2$. After dissolving the bromine in a strong solution of calcium bromide and precipitating with an excess of water, it loses all the chlorine it contained, because chlorine forms calcium chloride with CaBr_2 .

⁵⁹ There existed for long a difference of opinion as to the melting-point of pure bromine. By some investigators it was given as between -7° and -8° , and by others as between -20° and -25° . There is now no doubt, thanks to the researches of Ramsay and Young (1885), that pure bromine melts at about -7° . For solid bromine the vapour pressure p in mm. at t was found to be—

$p =$	20	25	30	35	40	45 mm.
$t =$	-16.6°	-14°	-12°	-10°	-8.5°	-7°

For liquid bromine—

$p =$	50	100	200	400	600	760 mm.
$t =$	-5.0°	$+8.2^\circ$	23.4°	40.4°	51.9°	58.7°

These curves intersect at -7.05° . Besides which, in comparing the vapour pressures of many liquids (for example, those given in Chap. II., note 27), Ramsay and Young observed that the ratio of the absolute temperatures ($t + 273$) corresponding with equal pressures *varies* for every pair of substances as a *rectilinear function* of t , and, therefore, for the above pressure p , Ramsay and Young determined the ratio of $t + 273$ for water and bromine, and found that the straight lines expressing these ratios for liquid and solid bromine intersect also at 7.05° ; thus, for example, for solid bromine—

$p =$	20	25	30	35	40	45
$273 + t =$	256.4	259	261	263	264.6	266
$273 + t' =$	295.3	299	302.1	304.8	307.2	309.3
$c =$	1.152	1.154	1.157	1.159	1.161	1.163

where t' indicates the temperature of water corresponding with a vapour pressure p , and c is the ratio of $273 + t'$ to $273 + t$. The magnitude of c is evidently expressed with great

of liquid bromine at 0° is 3.187, and at 15° about 3.0. The boiling-point of bromine is about 58.7° (Ramsay). Bromine, like chlorine, is soluble in water; 1 part of bromine at 5° requires 27 parts of water, and at 15° , 29 parts of water for its solution. The aqueous solution of bromine is of an orange colour, and when cooled to -2° yields crystals containing 10 molecules of water to 1 molecule of bromine.⁶⁰ Alcohol dissolves a greater quantity of bromine, and ether a still greater amount. But after a certain time products of the action of the bromine on these organic substances are formed in the solutions. Aqueous solutions of the bromides also absorb a large amount of bromine.

With respect to **iodine**, this is almost exclusively extracted from the mother liquors after the crystallisation of natural sodium nitrate (Chili saltpetre) and from the ashes of the seaweed cast upon the shores of France, Great Britain, and Spain, sometimes in considerable quantities, by the high tides. The majority of these seaweeds are of the genera *Fucus*, *Laminaria*, &c. The fused ashes of these seaweeds are called 'kelp' in Scotland and 'varech' in Normandy. A somewhat considerable quantity of iodine is contained in these seaweeds, and in sea-sponges (partly in the form of special organic compounds discovered by Gauthier, also in the air and in sea water, although in very small quantities). After being burnt (or subjected to dry distillation) an ash is left which contains chiefly salts of potassium, sodium, and calcium. The metals occur in the seaweed as salts of organic acids. On being burnt these organic salts are decomposed, forming carbonates of potassium and sodium. Hence, sodium carbonate is found in the ash of sea plants. The ash is dissolved in hot water, and on evaporation sodium carbonate and other salts separate, but a portion of the substances remains in solution. These mother liquors left after the separation of the sodium carbonate contain chlorine, bromine, and iodine in combination with metals, the chlorine and iodine being in excess

accuracy by the straight line, $c = 1.1703 + 0.0011t$. In exactly the same way we find the ratio for liquid bromine and water to be $c_1 = 1.1585 + 0.00057t$. The intersection of these straight lines also corresponds with -7.06° , which again confirms the melting-point given above for bromine. In this manner it is possible with the existing store of data to accurately establish and **verify** the melting-point of substances. Ramsay and Young established the thermal constants of iodine by exactly the same method.

⁶⁰ The observations made by Paterno and Nasini (by Raoult's method, Chap. I., note 49) on the temperature of the formation of ice (-1.115° , with 1.391 gram of bromine in 100 grams of water) in an aqueous solution of bromine, showed that bromine is contained in solutions as the molecule Br_2 . Similar experiments conducted on iodine (Kloboukoff, 1889, and Beckmann, 1890) show that in solution the molecule is I_2 .

B. Roozeboom investigated the hydrate of bromine as completely as the hydrate of chlorine (notes 9 and 10). The temperature of the complete decomposition of the hydrate is $+6.2^{\circ}$; the density of $\text{Br}_2 \cdot 10\text{H}_2\text{O}$ is 1.49.

over the bromine. Thirteen thousand kilos of kelp give about 1,000 kilos of sodium carbonate and 15 of iodine.

The liberation of the iodine from the mother liquor is effected with comparative ease, because chlorine disengages iodine from potassium iodide and its other combinations with the metals. Not only chlorine but also sulphuric acid liberate iodine from sodium iodide. Sulphuric acid, in acting on an iodide, sets free hydriodic acid, but the latter then decomposes (see further on), especially in the presence of substances capable of evolving oxygen, such as chromic acid, nitrous acid, or even ferric salts.⁶¹ Owing to its sparing solubility in water, the iodine liberated separates as a precipitate. To obtain pure iodine it is distilled, the first and last portions of the distillate being neglected and the middle portion only being collected. Iodine passes directly from a state of vapour into a crystalline form, and settles on the cool portions of the apparatus in tabular crystals, having a blackish-grey colour and metallic lustre.

The specific gravity of the crystals of iodine is 4.93 at 4°. It melts at 115.1° and boils at 183.05°. ⁶² Its vapour is formed at a much lower

⁶¹ In general, $2\text{HI} + \text{O} = \text{I}_2 + \text{H}_2\text{O}$, if the oxygen proceed from a substance from which it is easily evolved. For this reason compounds corresponding with the higher stages of oxidation or chlorination frequently give a lower stage when treated with hydriodic acid. Ferric oxide, Fe_2O_3 , is a higher oxide, and ferrous oxide, FeO , a lower oxide; the former corresponds with FeX_3 , and the latter with FeX_2 , and this passage from the higher to the lower takes place under the action of hydriodic acid. Thus hydrogen peroxide and ozone (Chap. IV.) are able to liberate iodine from hydriodic acid. Compounds of copper oxide, CuO or CuX_2 , give compounds of the suboxide Cu_2O , or CuX . Even sulphuric acid, which corresponds to the higher stage SO_3 , is able to act thus, forming the lower oxide SO_2 . The liberation of iodine from hydriodic acid proceeds with still greater ease under the action of substances capable of disengaging oxygen. In practice, many methods are employed for liberating iodine from acid liquids containing, for example, sulphuric acid and hydriodic acid. Nitrous acid and the higher oxides of nitrogen are most commonly used; they then pass into nitric oxide. Iodine may even be disengaged from hydriodic acid by the action of iodic acid, &c. But there is a limit in these reactions of the oxidation of hydriodic acid because, under certain conditions, especially in dilute solutions, the iodine set free is itself able to act as an oxidising agent—that is, it exhibits the character of the halogens. The iodine is liberated from iodates by acid sulphites, for instance: $2\text{NaIO}_3 + 3\text{Na}_2\text{SO}_3 + 2\text{NaHSO}_3 = \text{I}_2 + \text{H}_2\text{O} + 5\text{Na}_2\text{SO}_4$, that is, the iodic acid is reduced by the sulphurous acid, which passes into sulphuric acid. In Chili a mother liquor containing NaIO_3 is obtained in the extraction of nitre, and iodine is obtained from it in the above manner.

⁶² For the final purification of iodine, Stas dissolved it in a strong solution of potassium iodide, and precipitated it by the addition of water, while Ladenburg (1902) purified iodine in the form of a precipitate of AgI by shaking it up with an excess of a strong solution of ammonia, as 100 grams of ammonia only dissolve 0.0045 AgI at 16°, and the solubility of AgCl is 1,000 times greater. The iodine is converted into ZnI_2 by treating with pure zinc and sulphuric acid, and the action of nitrous acid upon the solution of ZnI_2 liberates the iodine. Ladenburg found that the atomic weight of this iodine was $\text{I} = 126.96$, while Stas gives that of the iodine he purified as $\text{I} = 126.85$, taking 0 as 16. Possibly Ladenburg's iodine yet retained some trace

temperature, and is of a violet colour, whence iodine receives its name (*ιοειδής*, violet-coloured). The smell of iodine recalls the characteristic smell of hypochlorous acid; it has a sharp, sour taste. It destroys the skin and organs of the body, and is therefore frequently employed for cauterising and as an irritant for the skin. In small quantities it turns the skin brown, but the coloration disappears after a certain time, partly owing to the volatility of the iodine. Water dissolves only $\frac{1}{5000}$ part of its weight of iodine. A brown solution is thus obtained, which bleaches, but much more feebly than either bromine or chlorine. Water which contains salts, and especially iodides, in solution dissolves iodine in increased quantities, and the resultant solution is of a dark brown colour. Alcohol and ether dissolve a small amount of iodine, and in so doing acquire a brown colour, but the solubility of iodine in alcohol is considerably increased by the presence of a small quantity of an iodine compound—for instance, ethyl iodide.⁶³ Solutions of iodine in carbon bisulphide and chloroform are rose colour, but with a larger proportion of iodine they assume a violet colour. The rose colour given by a small amount of iodine to chloroform is an easy means for detecting the presence of free iodine formed (for instance, by the action of Cl on KI). The blue coloration which free iodine gives with **starch** may also, as has already been frequently mentioned (see Chap. IV.), serve for the detection of iodine.

In reviewing the chief characteristics of the compounds formed by bromine and iodine, it is first of all seen that their composition and their physical and chemical properties are analogous to the corresponding chlorine compounds, and that they all vary in the same order with the atomic weight of the component haloid or molecular weight of the compound. Thus bromine introduces properties which stand as the mean of those communicated by chlorine and iodine. If the weight of

of chlorine or bromine, and this is all the more likely, as the drying was conducted with calcium chloride, and free iodine probably gives some traces of CaI_2 and Cl in the presence of CaCl_2 ; this would hence again introduce some chlorine into the iodine (see note 66). Traces of Cl and Br should diminish the atomic weight of the iodine, and therefore I think the true atomic weight cannot be less than 127 and probably even slightly above 127.

⁶³ The solubility of iodine in solutions containing iodides and compounds of iodine in general, may serve, on the one hand, as an indication that solution is due to a similarity between the solvent and dissolved substance, and, on the other, as an indirect proof of that view as to solutions which was cited in Chap. I., because in many instances unstable highly iodised compounds, resembling crystallo-hydrates, have been obtained from such solutions. Thus tetramethylammonium iodide, $\text{N}(\text{CH}_3)_4\text{I}$, combines with I_2 and I_4 . Even a solution of iodine in a saturated solution of potassium iodide presents indications of the formation of a definite compound KI_3 . Thus, an alcoholic solution of KI_3 does not give up iodine to carbon bisulphide, although this solvent takes up iodine from an alcoholic solution of iodine itself (Girault, Jørgensen, and others). See Chapter XIII., note 3a.

the molecule is large, the substance has a higher specific gravity and higher melting and boiling points. Chlorine in a free state boils at about -35° , bromine at 60° , and iodine only above 180° . According to the Avogadro-Gerhardt law, the vapour densities of these elements in a gaseous state are proportional to their atomic weights, and here, at all events approximately, the densities in a liquid (or solid) state are also almost in the ratio of their atomic weights. Dividing the atomic weight of chlorine (35.5) by its specific gravity in a liquid state (1.3), we obtain a volume of 27, for bromine ($80/3.1$) 26, and for iodine ($127/4.9$) 26.⁶⁴

Notwithstanding the great analogy of the bromides and iodides with the corresponding chlorides,⁶⁵ chlorine displaces their bromine or iodine, and bromine liberates iodine from iodides. However, the researches of Potilitzin (1880) showed that a **reverse** displacement of chlorine by bromine may occur both in solutions and in ignited metallic chlorides in an atmosphere of bromine vapour—that is, a distribution of the metal (according to Berthollet's doctrine) takes place between the halogens, although, however, the larger portion still unites with the chlorine, which shows its greater affinity for metals as compared with those of bromine and iodine.⁶⁶ The latter usually behave with respect

⁶⁴ The equality of the atomic volumes of the halogens themselves is all the more remarkable because in all the halogen compounds the volume increases with the substitution of fluorine by chlorine, bromine, and iodine. Thus, for example, the volume of sodium fluoride (obtained by dividing the weight expressed by its formula by its specific gravity) is about 15, that of sodium chloride 27, that of sodium bromide 32, and that of sodium iodide 41. The volume of silicon chloroform, SiHCl_3 , is 82, and those of the corresponding bromine and iodine compounds are 108 and 122 respectively.

⁶⁵ But the density (boiling-point, &c.) of a bromine compound is always greater than that of a chlorine compound, whilst that of an iodine compound is still greater.

⁶⁶ A. L. Potilitzin showed that on heating various metallic chlorides in a closed tube, with an equivalent quantity of bromine, a distribution of the metal between the halogens always occurs, and that the amounts of chlorine replaced by the bromine in the ultimate product are proportional to the atomic weights of the metals taken and inversely proportional to their equivalence. Thus, if $\text{NaCl} + \text{Br}$ be taken, then out of 100 parts of chlorine, 5.54 are replaced by the bromine, whilst with $\text{AgCl} + \text{Br}$, 27.28 parts are replaced. These figures are in the ratio 1 : 4.9, and the atomic weights $\text{Na} : \text{Ag}$ are as 1 : 4.7. In general terms, if a chloride MCl_n be taken, it gives with $n\text{Br}$ a percentage substitution of $4M/n^2$, where M is the atomic weight of the metal. This law was deduced from observations on the chlorides of Li , K , Na , Ag ($n=1$), Ca , Sr , Ba , Co , Ni , Hg , Pb ($n=2$), Bi ($n=3$), Sn ($n=4$), and Fe_2 ($n=6$).

In these determinations of **Potilitzin** we see not only a brilliant confirmation of *Berthollet's doctrine*, but also a new effort to determine the affinities of elements. The chief object of these researches consisted in proving whether a displacement occurs in those cases where heat is absorbed, and in this instance it should be absorbed, because the formation of all metallic bromides is attended with the evolution of less heat than that of the chlorides, as is seen by the figures given in note 55.

If the mass of the bromine be increased, then the amount of chlorine displaced also increases. For example, if masses of bromine of 1 and 4 equivalents act on a molecule

to metallic oxides in exactly the same manner as chlorine. Gay-Lussac, by igniting potassium carbonate in iodine vapour, obtained (as with chlorine) an evolution of oxygen and carbonic anhydride, $\text{K}_2\text{CO}_3 + \text{I}_2 = 2\text{KI} + \text{CO}_2 + \text{O}$, only the reactions between the halogens and oxygen are more easily reversible with bromine and iodine than with chlorine. Thus, at a red heat, oxygen displaces iodine from barium iodide. Aluminium iodide burns in a current of oxygen (Deville and Troost), and a similar, although not so clearly marked, relation exists for aluminium chloride, and shows that the halogens have a distinctly smaller affinity for those metals which form feeble bases. This is still more the case with the non-metals, which form acids and evolve much more heat with oxygen than with the halogens (note 13). But in all these instances the affinity (and amount of heat evolved) of iodine and bromine is less than that of chlorine, because the atomic weights are greater. The smaller store of energy in iodine and bromine is seen still more clearly in the relation of the halogens to hydrogen. In a gaseous state they all enter, with more or less ease, into direct combination with gaseous hydrogen—for example, in the presence of spongy platinum, forming halogen acids, HX —but the latter are far from being equally stable; hydrogen chloride is the most stable and hydrogen iodide the least so, hydrogen bromide occupying an intermediate position. A very high temperature is required to decompose hydrogen chloride even partially, whilst hydrogen iodide is decomposed by light even at the ordinary temperature and very easily at a red heat. Hence the reaction, $\text{I}_2 + \text{H}_2 = \text{HI} + \text{HI}$, is very easily reversible, and hydrogen iodide easily dissociates.⁶⁷ Judging by the direct measurement of the heat evolved

of sodium chloride, then the percentages of the chlorine displaced will be 6.08 per cent. and 12.46 per cent. respectively; in the action of 1, 4, 25, and 100 molecules of bromine on a molecule of barium chloride, there will be displaced 7.8, 17.6, 35.0, and 45.0 per cent. respectively of chlorine. If an equivalent quantity of hydrochloric acid act on metallic bromides in closed tubes, and in the absence of water at a temperature of 300° , the percentages of the substitution of the bromine by the chlorine in the double decomposition taking place between univalent metals are inversely proportional to their atomic weights. For example, $\text{NaBr} + \text{HCl}$ gives at the limit 21 per cent. of displacement, KCl 12 per cent., and AgCl $4\frac{1}{4}$ per cent. Essentially the same action takes place in an aqueous solution, although the phenomenon is complicated by the participation of the water. The reactions proceed spontaneously in one or the other direction at the ordinary temperature but at different rates. In the action of a dilute solution (1 equivalent per 5 litres) of sodium chloride on silver bromide at the ordinary temperature, the amount of bromine replaced in six and a half days is 2.07 per cent., and with potassium chloride 1.5 per cent. With an excess of the chloride the magnitude of the substitution increases. These conversions also proceed with the absorption of heat. The reverse reactions, evolving heat, proceed incomparably more rapidly, but also have a certain limit.

⁶⁷ **The dissociation of hydriodic acid** has been studied in detail by Hautefeuille and Lemoine, from whose researches we extract the following information. The decomposition of hydriodic acid is appreciable but slow at 180° ; the rate and limit of

(22,000 heat units) in the formation of HCl , the conversion of 2HCl into $\text{H}_2 + \text{Cl}_2$ requires the expenditure of 44,000 heat units. The decomposition of 2HBr into $\text{H}_2 + \text{Br}_2$ only requires, if the bromine be obtained in a gaseous state, a consumption of about 24,000 units, whilst in the decomposition of 2HI into $\text{H}_2 + \text{I}_2$ as vapour about 3,000 heat units are *evolved*; ⁶⁸ these facts, without doubt, stand in causal

decomposition increase with a rise of temperature. The reverse action—that is, $\text{I}_2 + \text{H}_2 = 2\text{HI}$ —proceeds not only under the influence of spongy platinum (Corenwinder), which also accelerates the decomposition of hydriodic acid, but also by itself, although slowly. The limit of the reverse reaction is the same either with or without spongy platinum. An increase of pressure has a very powerful accelerative effect on the rate of formation of hydriodic acid, and therefore spongy platinum by condensing gases has the same effect as increase of pressure. At the atmospheric pressure the decomposition of hydriodic acid reaches the limit at 250° in several months, and at 440° in several hours. The limit at 250° is about 18 per cent. of decomposition—that is, out of 100 parts of hydrogen previously combined in hydriodic acid, about 18 may be disengaged at this temperature (this hydrogen may be easily measured, and the degree of dissociation determined), but not more; the limit at 440° is about 26 per cent. If the pressure under which 2HI passes into $\text{H}_2 + \text{I}_2$ is $4\frac{1}{2}$ atmospheres, then the limit is 24 per cent.; under a pressure of $\frac{1}{5}$ atmosphere the limit is 29 per cent. The small influence of pressure on the dissociation of hydriodic acid (compared with that of N_2O_4 , Chap. VI., note 46) is due to the fact that the reaction $2\text{HI} = \text{I}_2 + \text{H}_2$ is not accompanied by a change of volume. In order to show the influence of time, we shall cite the following figures referring to 350° : (1) Reaction $\text{H}_2 + \text{I}_2$: after 3 hours, 88 per cent. of hydrogen remained free; after 8 hours, 69 per cent.; 34 hours, 48 per cent.; 76 hours, 29 per cent.; and after 327 hours, 18.5 per cent. (2) The reverse decomposition of 2HI : after 9 hours, 3 per cent. of hydrogen was set free, and after 250 hours, 18.6 per cent.—that is, the limit was reached. The addition of extraneous hydrogen diminishes the limit of the reaction of decomposition, or increases the formation of hydriodic acid from iodine and hydrogen, as would be expected from Berthollet's doctrine (Chap. X.). Thus at 440° , 26 per cent. of hydriodic acid is decomposed if there be no admixture of hydrogen, while if H_2 be added, then at the limit only half as large a mass of HI is decomposed. Therefore, if an infinite mass of hydrogen be added there will be no decomposition of the hydriodic acid. Light aids the decomposition of hydriodic acid very powerfully. At the ordinary temperature 80 per cent. is decomposed under the influence of light, whilst under the influence of heat alone this limit corresponds with a very high temperature. The distinct action of light, spongy platinum, and of impurities in the glass (especially of sodium sulphate, which decomposes hydriodic acid), not only render the investigations difficult, but also show that in reactions like $2\text{HI} = \text{I}_2 + \text{H}_2$, which are accompanied by slight heat effects, all foreign and feeble influences may strongly affect the progress of the action (note 47).

⁶⁸ The thermal determinations of Thomsen (at 18°) gave, in thousands of calories, $\text{Cl} + \text{H} = +22$; $\text{HCl} + \text{Aq}$ (that is, on dissolving HCl in a large amount of water) $= +17.3$, and therefore $\text{H} + \text{Cl} + \text{Aq} = +39.3$. In taking molecules, all these figures must be doubled. $\text{Br} + \text{H} = +8.4$; $\text{HBr} + \text{Aq} = 19.9$; $\text{H} + \text{Br} + \text{Aq} = +28.3$. According to Berthelot, 7.2 are required for the vaporisation of Br_2 , hence $\text{Br}_2 + \text{H}_2 = 16.8 + 7.2 = +24$, if Br_2 is taken as vapour for comparison with Cl_2 . $\text{H} + \text{I} = -6.0$, $\text{HI} + \text{Aq} = 19.2$; $\text{H} + \text{I} + \text{Aq} = +13.2$, and, according to Berthelot, the heat of fusion of $\text{I}_2 = 3.0$, and that of vaporisation 6.0 thousand heat units, and therefore $\text{I}_2 + \text{H}_2 = -2(6.0) + 3 + 6 = -3.0$, if the iodine be taken as vapour. Berthelot, on the basis of his determinations, gives, however, +0.8 thousand heat unit. Similar contradictory results are often met with in thermochemistry owing to the imperfection of the existing methods, and particularly to the necessity of depending on indirect methods for obtaining the fundamental figures. Thus

connection with the great stability of hydrogen chloride, the easy decomposability of hydrogen iodide, and the intermediate properties of hydrogen bromide. From this it would be expected that chlorine is capable of decomposing water with the evolution of oxygen, whilst iodine has not the energy to produce this disengagement,⁶⁹ although it is able to liberate the oxygen from the oxides of potassium and sodium, the affinity of these metals for the halogens being very considerable. For this reason oxygen, especially in compounds from which it can be readily evolved (for instance, ClHO , CrO_3 , &c.), readily decomposes hydrogen iodide. A mixture of hydrogen iodide and oxygen burns in the presence of an ignited substance, forming water and iodine. Drops of nitric acid in an atmosphere of hydrogen iodide cause the disengagement of violet fumes of iodine and brown fumes of nitrogen peroxide. In the presence of alkalies and an excess of water, however, iodine is able to effect oxidation like chlorine—that is, it decomposes water; the action is here aided by the affinity of hydrogen iodide for the alkali and water, just as sulphuric acid helps zinc to decompose water. But the relative instability of hydriodic acid is best seen in comparing the acids in a gaseous state. If the halogen acids be dissolved in water, they evolve so much heat that they approach much nearer to each other in properties. This is seen from thermochemical data, for in the formation of HX in solution (in a large excess of water) from the *gaseous* elements, there is *evolved* for HCl 39,000, for HBr 32,000, and for HI 18,000 heat units;⁷⁰ but it is especially evident from the fact that solutions of hydrogen bromide and iodide in water have many points in common with solutions of hydrogen chloride, even in their capacity to form hydrates and fuming solutions of constant boiling-point.

In consequence of what has been said above, it follows that **hydro-**

Thomsen decomposed a dilute solution of potassium iodide by gaseous chlorine; the reaction gave +26·2, whence, having first determined the heat effects of the reactions $\text{KHO} + \text{HCl}$, $\text{KHO} + \text{HI}$ and $\text{Cl} + \text{H}$ in aqueous solutions, it was possible to find $\text{H} + \text{I} + \text{Aq}$; then, knowing $\text{HI} + \text{Aq}$, to find $\text{I} + \text{H}$. It is evident that unavoidable errors may accumulate.

⁶⁹ One can believe, however, on the basis of Berthollet's doctrine, and the observations of Potilitzin (note 66), that a certain slow decomposition of water by iodine takes place. According to this view, the observations of Dossios and Weith showing that the solubility of iodine in water increases after the lapse of several months, will be comprehensible. Hydriodic acid is then formed, and increases the solubility. If the iodine be extracted from such a solution by means of carbon bisulphide, then, as the authors showed, after the action of nitrous anhydride, iodine may be again detected in the solution by means of starch. It can easily be understood that a number of similar reactions, requiring much time and taking place to a slight extent, have up to now eluded the attention of investigators, who even still doubt the universal application of Berthollet's doctrine, or only see the thermochemical side of reactions, or else neglect to pay attention to the element of time and the influence of mass.

⁷⁰ On the basis of the data given in note 68.

bromic and hydriodic acids, being substances which are but slightly stable, cannot be evolved in a gaseous state under many of those conditions under which hydrochloric acid is formed. Thus if sulphuric acid in solution acts on sodium iodide, all the same phenomena take place as with sodium chloride; but if sodium iodide be mixed with strong sulphuric acid, then the oxygen of the latter decomposes the hydriodic acid set free, with liberation of iodine, $\text{H}_2\text{SO}_4 + 2\text{HI} = 2\text{H}_2\text{O} + \text{SO}_2 + \text{I}_2$. This reaction takes place in the reverse direction in the presence of a *large quantity* of water (2,000 parts of water per 1 part of SO_2), in which case not only is the affinity of hydriodic acid for water brought to light, but also the action of water in directing chemical reactions in which it participates.⁷¹ Therefore, with a halogen salt, it is easy to obtain gaseous hydrochloric acid by the action of sulphuric acid, but neither hydrobromic nor hydriodic acid can be so obtained in the free state (as gases).⁷² Other methods have to be resorted to for their preparation, and recourse must not be had to compounds of oxygen, which are so easily able to destroy these acids. Therefore hydrogen sulphide, phosphorus, &c., which themselves easily take up oxygen, lead to the conversion of bromine and iodine into hydrobromic and hydriodic acids in the presence of water. For example, in the action of phosphorus the essence of the matter is that the oxygen of the water goes to the phosphorus, and the union of the remaining elements leads to the formation of hydrobromic or hydriodic acid; but the matter is complicated by the reversibility of the reaction, the affinity for water, and other circumstances which are understood by following Berthollet's doctrine. Chlorine (and bromine also) directly decomposes hydrogen sulphide, forming hydrochloric acid and liberating sulphur, both in a gaseous form and in solutions, whilst iodine only decomposes hydrogen sulphide in weak solutions, when its affinity for hydrogen is aided by the affinity of hydrogen iodide for water. In a gaseous state iodine does not act on hydrogen sulphide,⁷³ whilst sulphur is able to decompose gaseous hydriodic acid, forming hydrogen sulphide and a compound of sulphur and iodine which with water forms hydriodic acid.⁷⁴

⁷¹ A number of similar cases confirm what has been said in Chap. X.

⁷² This is prevented by the reducibility of sulphuric acid. If volatile acids be taken they pass over, together with the hydrobromic and hydriodic acids, when distilled; whilst many non-volatile acids which are not reduced by hydrobromic and hydriodic acids only act feebly (like phosphoric acid), or do not act at all (like boric acid).

⁷³ This is in agreement with the thermochemical data, because if all the substances are taken in the gaseous state (for sulphur the heat of fusion is 0.3, and the heat of vaporisation 2.3) we have $\text{H}_2 + \text{S} = 4.7$; $\text{H}_2 + \text{Cl}_2 = 44$; $\text{H}_2 + \text{Br}_2 = 24$, and $\text{H}_2 + \text{I}_2 = -3$ thousand heat units; hence the formation of H_2S gives less heat than that of HCl and HBr , but more than that of HI .

⁷⁴ Here there are three elements, hydrogen, sulphur, and iodine, each pair of which is able to form a compound, HI , H_2S , and SI , besides which the latter may unite in

If hydrogen sulphide be passed through water containing iodine, the reaction $\text{H}_2\text{S} + \text{I}_2 = 2\text{HI} + \text{S}$ proceeds so long as the solution is dilute; but when the mass of free HI increases the reaction stops, because the iodine then passes into solution.^{74a}

To obtain⁷⁵ gaseous hydrobromic and hydriodic acids it is most convenient to take advantage of the reactions between phosphorus, the halogens, and water, the latter being present in small quantity (otherwise the halogen acids formed are dissolved by it); the halogen is gradually added to the phosphorus moistened with water. Thus, if red phosphorus be placed in a flask and moistened with water, and bromine be added drop by drop (from a tap funnel), hydrobromic acid will be abundantly and uniformly disengaged.⁷⁶ Hydrogen iodide is prepared

various proportions. The complexity of chemical mechanics is seen in such examples as these. It is evident that only the study of the simplest cases can give the key to the more complex problems, and on the other hand it is evident from the examples cited in the last pages that, without penetrating into the conditions of chemical equilibria, it would be impossible to explain chemical phenomena. By following the footsteps of Berthollet the possibility of unravelling these problems will be reached; but work in this direction has only been begun during the last ten years, and much remains to be done in collecting experimental material, for which occasions present themselves at every step. In speaking of the halogens I wished to turn the reader's attention to problems of this kind.

^{74a} A solution having a composition approximating to $2\text{HI} + 4\text{I}_2 + 9\text{H}_2\text{O}$ (according to Bineau) does not react with H_2S , notwithstanding the quantity of free iodine. Therefore only weak solutions of hydriodic acid can be obtained by passing hydrogen sulphide into water with iodine. Essentially the same thing takes place when sulphurous anhydride, in a dilute solution, gives hydriodic acid and sulphuric acid with iodine. On concentration a reverse reaction takes place. The equilibrated systems and the part played by water are everywhere distinctly seen.

⁷⁵ Methods of formation and preparation are nothing more than particular cases of chemical reaction. If the knowledge of chemical mechanics were more complete than it now is, it would be possible to foretell all cases of preparation *with every detail* (of the quantity of water, temperature, pressure, mass, &c.). The study of practical methods of preparation is therefore one of the paths for the study of chemical mechanics. The action of iodine on phosphorus and water is a case like that mentioned in note 74, and the matter is here further complicated by the possibility of the formation of the compound PH_3 with HI, as well as the production of PI_2 , PI_3 , and the affinity of hydriodic acid and the acids of phosphorus for water. The theoretical interest of equilibria in all their complexity is naturally very great, but it falls into the background in presence of the primary interest of discovering practical methods for the isolation of substances, and the means of employing them for the requirements of man. It is only after the satisfaction of these requirements that interests of the other order arise, which in their turn must exert an influence on the former. For these reasons, whilst considering it opportune to point out the theoretical interest of chemical equilibria, the chief attention of the reader is directed in this work to questions of practical importance, as it is chiefly designed for beginners and to awaken in them an interest in the whole of chemistry.

⁷⁶ Hydrobromic acid is also obtained by the action of bromine on paraffin heated to 180° , and on other hydrocarbons. The liquid tribromide of phosphorus, directly obtained from phosphorus and bromine, also gives hydrobromic acid when treated with water. Bromide of potassium or sodium, when treated with sulphuric acid in the presence of phosphorus, also gives hydrobromic acid, but hydriodic acid is decomposed by this method. In order to free hydrobromic acid from bromine vapour it is passed over moist

by adding 1 part of common (yellow) dry phosphorus to 10 parts of dry iodine in a glass flask. On shaking the flask, union proceeds quietly between them (light and heat being evolved), and when the mass of iodide of phosphorus which is formed has cooled, water is added, drop by drop (from a tap funnel) and hydrogen iodide is evolved directly without the aid of heat. These methods of preparation will be at once understood when it is remembered that phosphorus chloride gives hydrogen chloride with water. It is exactly the same here—the oxygen of the water passes over to the phosphorus, and the hydrogen to the iodine; thus, $\text{PI}_3 + 3\text{H}_2\text{O} = \text{PH}_3\text{O}_3 + 3\text{HI}$.⁷⁷

In the gaseous state hydrobromic and hydriodic acids are closely analogous to hydrochloric acid; they are liquefied by pressure and cold, they fume in the air, form solutions and hydrates of constant boiling-point, and react on metals, oxides and salts, &c.⁷⁸ Only the relatively

phosphorus and then dried either by phosphoric anhydride or calcium bromide (calcium chloride cannot be used, as hydrochloric acid would be formed). Neither hydrobromic nor hydriodic acid can be collected over mercury, on which they act, but they may be directly collected in a dry vessel by leading the gas-conducting tube to the bottom of the vessel, both gases being much heavier than air. Merz and Holtzmann (1889) propose to prepare HBr directly by heating a mixture of vapour of Br with H. According to the method proposed by Newth (1892) a mixture of bromine and hydrogen is led through a tube containing a platinum spiral, which is heated to redness after the air has been displaced from the tube.

Hydriodic acid is obtained in the same manner as hydrobromic. Iodine is heated in a small flask, and its vapour is carried over by hydrogen into a strongly heated tube. The gas passing from the tube is found to contain a considerable amount of HI, together with some free iodine. At a low red heat about 17 per cent. of the iodine vapour enters into combination; at a higher temperature, 78 to 79 per cent.; and at a strong heat about 82 per cent.

⁷⁷ But generally more phosphorus is taken than is required for the formation of PI_3 , because otherwise a portion of the iodine distils over. If less than one-tenth part of iodine be taken, much phosphonium iodide, PH_4I , is formed. This proportion was established by Gay-Lussac and Kolbe. Hydriodic acid is also prepared in many other ways. Bannoff dissolves two parts of iodine in one part of a previously prepared strong (sp. gr. 1.67) solution of hydriodic acid, and pours it on to red phosphorus in a retort. In taking P and I it must be remembered that reverse reaction (Oppenheim) may take place between the hydriodic acid and phosphorus, in which the compounds PH_4I and PI_2 are formed.

The reaction between phosphorus, iodine, and water must be carried out with caution, as they may react with explosion. With red phosphorus the reaction proceeds quietly, but nevertheless requires care. L. Meyer showed that with an excess of iodine the reaction proceeds without the formation of by-products (PH_4I), according to the equation, $\text{P} + 5\text{I} + 4\text{H}_2\text{O} = \text{PH}_3\text{O}_4 + 5\text{HI}$. For this purpose 100 grams of iodine and 10 grams of water are placed in a retort, and a paste of 5 grams of red phosphorus and 10 grams of water is added little by little (at first with great care).

⁷⁸ The specific gravities of their solutions, as deduced by me on the basis of Topsøe and Berthelot's determinations for $15^\circ/4^\circ$, are as follows:—

	10	20	30	40	50	60 per cent.
HBr	1.071	1.156	1.258	1.374	1.505	1.650
HI	1.075	1.164	1.267	1.399	1.567	1.769

Hydrobromic acid forms two hydrates, $\text{HBr} \cdot 2\text{H}_2\text{O}$ and $\text{HBr} \cdot \text{H}_2\text{O}$, which have been

ready decomposability of hydrobromic acid, and especially of hydriodic acid, clearly distinguish these acids from hydrochloric acid. For this reason, hydriodic acid acts in a number of cases as a deoxidiser or reducer, and frequently even serves as a means for the transference of hydrogen. Thus Berthelot, Baeyer, Wreden, and others, by heating unsaturated hydrocarbons in a solution of hydriodic acid, obtained either compounds with hydrogen nearer to the limit C_nH_{2n+2} or even the saturated compounds themselves. For example, benzene, C_6H_6 , when heated in a closed tube with a strong solution of hydriodic acid, gives hexylene, C_6H_{12} . The ready decomposability of hydriodic acid accounts for the fact that iodine does not act by metalepsis on hydrocarbons, for the hydrogen iodide liberated gives with the product of metalepsis, RI , formed, iodine and the hydrogen compound, RH , again. And therefore, to obtain the products of iodine substitution, either iodic acid, HIO_3 (Kekulé), or mercuric oxide, HgO (Weselsky), is added, as these immediately react on the hydrogen iodide, thus: $HIO_3 + 5HI = 3H_2O + 3I_2$, or, $HgO + 2HI = HgI_2 + H_2O$. From these considerations it will readily be understood that iodine acts like chlorine (or bromine) on ammonia and sodium hydroxide, for in these cases the hydriodic acid produced forms NH_4I and NaI . With a solution of iodine in alcohol, or even the solid element, ammonia immediately forms a highly explosive solid black product of metalepsis, NHI_2 , generally known as **iodide of nitrogen**, although it still contains hydrogen (this was proved beyond doubt by Szuhay, 1893), which may be replaced by silver (with the formation of $NAgI_2$): $3NH_3 + 2I_2 = 2NH_4I + NHI_2$. However, the composition of the last product is variable, and with an excess of water, NI_3 seems to be formed. Iodide of nitrogen is just as explosive as nitrogen chloride.^{78a} In the action of iodine on sodium hydroxide no bleaching

studied by Roozeboom with as much completeness as the hydrate of hydrochloric acid (Chap. X., note 37).

With metallic silver, solutions of hydriodic acid give hydrogen with great ease, forming silver iodide. Mercury, lead, and other metals act in a similar manner.

^{78a} Iodide of nitrogen, NHI_2 , is obtained as a brown pulverulent precipitate on adding a solution of iodine (in alcohol, for instance) to a solution of ammonia. If it be collected on a filter-paper, it does not decompose so long as the precipitate is moist; but when dry it explodes violently, so that it can only be experimented upon in small quantities. Usually the filter-paper is torn into bits while moist, and the pieces laid upon a brick; on drying an explosion proceeds, not only from friction or a blow, but even spontaneously. The more dilute the solution of ammonia, the greater is the amount of iodine required for the formation of the precipitate of NHI_2 . A low temperature facilitates its formation. NHI_2 dissolves in ammonia water, and when heated, the solution forms HIO_3 and iodine. With KI , iodide of nitrogen gives iodine, NH_3 and KHO . These reactions (Selivanoff) are explained by the formation of HIO , thus: $NHI_2 + 2H_2O = NH_3 + 2HIO$ and then $KI + HIO = I_2 + KHO$. Selivanoff (see note 29) usually observed a temporary formation of hypiodous acid, HIO , in the reaction of ammonia upon iodine, so that here the formation of NHI_2 is preceded by that of HIO —i.e., first $I_2 + H_2O = HIO + HI$, and then

compound is formed (whilst bromine gives one), but a direct reaction is always accomplished with the formation of an iodate, $6\text{NaHO} + 3\text{I}_2 = 5\text{NaI} + 3\text{H}_2\text{O} + \text{NaIO}_3$ (Gay-Lussac). Solutions of other alkalies, and even a mixture of water and oxide of mercury, act in the same manner.⁷⁹ This direct formation of **iodic acid**, $\text{HIO}_3 = \text{IO}_2(\text{OH})$, shows the propensity of iodine to give compounds of the type IX_5 . Indeed, this capacity of iodine to form compounds of a high type emphasises itself in many ways; for instance, with fluorine it directly forms IF_4 . But it is most important to turn attention to the fact that iodic acid is easily and directly formed by the action of oxidising substances on iodine. Thus, for instance, strong nitric acid directly converts iodine into iodic acid, whilst it has no oxidising action on chlorine.^{79a} This shows a greater affinity for oxygen in iodine than in chlorine, and this conclusion is confirmed by the fact that iodine displaces chlorine from its oxygen acids,⁸⁰ and that in the presence of water chlorine oxidises iodine.⁸¹

not only does the HI combine with NH_3 , but also $2\text{HIO} + \text{NH}_3 = \text{NHI}_2 + 2\text{H}_2\text{O}$. With dilute sulphuric acid, iodide of nitrogen (like NCl_3) forms hypoiodous acid, but it immediately passes into iodic acid.

⁷⁹ Free hypoiodous acid, HIO , is not known (see note 78a), but organic compounds, RIO , of the same type are known. To illustrate the peculiarities of their properties we will mention one of these compounds, namely, *iodosobenzene*, $\text{C}_6\text{H}_5\text{IO}$, obtained by Willgerodt (1892) and others, by the action of caustic alkalies upon phenyliododichloride, $\text{C}_6\text{H}_5\text{ICl}_2$ (according to the equation, $\text{C}_6\text{H}_5\text{ICl}_2 + 2\text{MOH} = \text{C}_6\text{H}_5\text{IO} + 2\text{MCl} + \text{H}_2\text{O}$). Iodosobenzene is an amorphous yellow substance; it explodes at 210° , decomposing with the evolution of iodine vapour, and dissolves in hot water and alcohol. If acids do not oxidise $\text{C}_6\text{H}_5\text{IO}$, they give saline compounds in which iodosobenzene appears as a basic oxide of a diatomic metal, $\text{C}_6\text{H}_5\text{I}$. Thus, for instance, when an acetic acid solution of iodosobenzene is treated with a solution of nitric acid, it gives large monoclinic crystals of a nitric acid salt having the composition $\text{C}_6\text{H}_5(\text{NO}_3)_2$ [like $\text{Ca}(\text{NO}_3)_2$]. Iodosobenzene displaces iodine from potassium iodide (in a solution acidulated with acetic or hydrochloric acid)—i.e., it acts with its oxygen like HClO . The action of peroxide of hydrogen, chromic acid, and other similar oxidising agents gives $\text{C}_6\text{H}_5\text{IO}_2$, which is a neutral substance—i.e., is incapable of giving salts with acids (compare Chap. XIII., note 43).

^{79a} The oxidation of iodine by strong nitric acid was discovered by Connell; Millon showed that it is effected, although more slowly, by the action of the hydrates of nitric acid up to $\text{HNO}_3, \text{H}_2\text{O}$, but that the solution $\text{HNO}_3, 2\text{H}_2\text{O}$, and weaker ones, do not oxidise, but simply dissolve, iodine. The participation of water in reactions is seen in this instance. It is also seen, for example, in the fact that dry ammonia combines directly with iodine—for instance, at 0° forming the compound $\text{I}_2, 4\text{NH}_3$ —whilst iodide of nitrogen is only formed in presence of water.

⁸⁰ Bromine also displaces chlorine—for instance, from chloric acid, directly forming bromic acid. If a solution of potassium chlorate is taken (75 parts per 400 parts of water), and iodine is added to it (80 parts), and then a small quantity of nitric acid, chlorine is disengaged on boiling, and potassium iodate formed in the solution. In this instance the nitric acid first evolves a certain portion of the chloric acid, and the latter, with the iodine, evolves chlorine. Potilitzin (1887) remarked, however, that not only do bromine and iodine displace the chlorine from chloric acid and potassium chlorate, but also that chlorine displaces bromine from sodium bromate, and, furthermore, the reaction does not proceed as a direct substitution of the halogens, but it is accompanied by the formation of free acids; for example, $5\text{NaClO}_3 + 3\text{Br}_2 + 3\text{H}_2\text{O} = 5\text{NaBr} + 5\text{HClO}_3 + \text{HBrO}_3$.

⁸¹ If iodine be stirred up in water, and chlorine passed through the mixture, the

Even ozone or a silent discharge passed through a mixture of oxygen and iodine vapour is able to directly oxidise iodine⁸² into iodic acid. It is disengaged from solutions as a hydrate, HIO_3 , which loses water at 170° , and gives an anhydride, I_2O_5 . Both these substances are crystalline (sp. gr. of I_2O_5 , 5.037, and of HIO_3 , 4.869 at 0°), colourless and soluble in water;⁸³ both decompose at a red heat into iodine and oxygen, are in many cases powerfully oxidising—for instance, they oxidise sulphurous anhydride, hydrogen sulphide, carbonic oxide, (Ditte) &c.—form chloride of iodine and water with hydrochloric acid, and with bases form salts, not only the normal, MIO_3 , but also acid salts; for example, KIO_3 , HIO_3 , and $\text{KIO}_3 \cdot 2\text{HIO}_3$.^{83a} With hydriodic acid, iodic acid immediately reacts, disengaging iodine, $\text{HIO}_3 + 5\text{HI} = 3\text{H}_2\text{O} + 3\text{I}_2$.

As with chlorine, so with iodine, a **periodic acid**, HIO_4 , is formed. This acid is produced in the form of its salts by the action of chlorine on alkaline solutions of iodates, and also by the action of iodine on chloric acid.⁸⁴ It crystallises from solutions as a hydrate containing

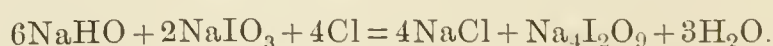
iodine will be dissolved; the liquid becomes colourless, and contains, according to the relative amounts of water and chlorine, either IHCl_2 , or ICl_3 , or HIO_3 . If there be a small amount of water, then the iodic acid may separate out directly as crystals, but a complete conversion (Bornemann) only occurs when not less than ten parts of water are taken to one part of iodine— $\text{ICl} + 3\text{H}_2\text{O} + 2\text{Cl}_2 = \text{HIO}_3 + 5\text{HCl}$. In general water must not be regarded simply as a 'medium' but as a chemical agent. In my opinion those who neglect this fact, especially from the consideration of dilute solutions, deny the lessons of Berthollet's law and fall into the dreams of Bergmann.

⁸² Schönbein and Ogier proved this. Ogier found that, at 45° , ozone immediately oxidises iodine vapour, forming first of all the oxide I_2O_3 , which is decomposed, by water or on heating, into iodic anhydride and iodine. Iodic acid is formed at the positive pole when a solution of hydriodic acid is decomposed by a galvanic current (Riche). It is also formed in the combustion of hydrogen mixed with a small quantity of hydriodic acid (Salet).

⁸³ Kämmerer showed that a solution of sp. gr. 2.127 at 14° , containing $2\text{HIO}_3 \cdot 9\text{H}_2\text{O}$, solidified completely in the cold. On comparing solutions $\text{HI} + m\text{H}_2\text{O}$ with $\text{HIO}_3 + m\text{H}_2\text{O}$, we find that the specific gravity increases but the volume decreases, whilst in the passage of solutions $\text{HCl} + m\text{H}_2\text{O}$ to $\text{HClO}_3 + m\text{H}_2\text{O}$, both the specific gravity and the volume increase, which is also observed in certain other cases (for example, H_3PO_3 and H_3PO_4).

^{83a} Ditte (1890) obtained many iodates of great variety. A neutral salt, $2(\text{LiIO}_3) \cdot \text{H}_2\text{O}$, is obtained by saturating a solution of lithia with iodic acid. There is an analogous ammonium salt, $2(\text{NH}_4\text{IO}_3) \cdot \text{H}_2\text{O}$. He also obtained hydrates of a more complex composition, such as $6(\text{NH}_4\text{IO}_3) \cdot \text{H}_2\text{O}$ and $6(\text{NH}_4\text{IO}_3) \cdot 2\text{H}_2\text{O}$. Salts of the alkaline earths, $\text{Ba}(\text{IO}_3)_2 \cdot \text{H}_2\text{O}$ and $\text{Sr}(\text{IO}_3)_2 \cdot \text{H}_2\text{O}$, may be obtained by a reaction of double decomposition from the normal salts of the type $2(\text{MeIO}_3) \cdot \text{H}_2\text{O}$. A mixture of solutions of nitrate of zinc and an alkaline iodate precipitates $\text{Zn}(\text{IO}_3)_2 \cdot 2\text{H}_2\text{O}$.

⁸⁴ If a mixture of sodium iodate with a solution of sodium hydroxide is heated, and chlorine passed through the solution, a sparingly soluble salt separates out, which corresponds with **periodic acid**, and has the composition $\text{Na}_4\text{I}_2\text{O}_9 \cdot 3\text{H}_2\text{O}$:



This compound is sparingly soluble in water, but dissolves easily in a very dilute solution of nitric acid. If silver nitrate is added to this solution a precipitate is formed

$2\text{H}_2\text{O}$ (corresponding with $\text{HClO}_4, 2\text{H}_2\text{O}$); but as it forms salts containing up to five atoms of metals, this water must be regarded as water of constitution. Therefore $\text{IO}(\text{OH})_5 = \text{HIO}_4, 2\text{H}_2\text{O}$ corresponds with the highest form of halogen compounds, IX_7 .⁸⁵ In decomposing (at 200°) or acting as an oxidiser, periodic acid first gives iodic acid, but it may also be ultimately decomposed.

Compounds formed between chlorine and iodine must be classed among the most interesting halogen bodies.⁸⁶ These elements combine together directly with evolution of heat, and form **iodine monochloride**, ICl , or **iodine trichloride**, ICl_3 .⁸⁷ As water reacts on these substances, forming iodic acid and iodine, they have to be prepared

which consists of the corresponding compound of silver, $\text{Ag}_4\text{I}_2\text{O}_9, 3\text{H}_2\text{O}$. If this sparingly soluble silver compound be dissolved in hot nitric acid, orange crystals of a salt having the composition AgIO_4 separate on evaporation.

The composition of all the salts of periodic acids are expressed by this type IX_7 . Kimmins (1889) refers all the salts of periodic acid to four types—the meta-salts of HIO_4 (salts of Ag, Cu, Pb), the meso-salts of H_3IO_5 (Pb, Ag_2H , CdH), the para-salts of H_5IO_6 (Na_2H_3 , Na_3H_2), and the di-salts of $\text{H}_4\text{I}_2\text{O}_9$ (K_4 , Ag_4 , Ni_2). The first three are direct compounds of the type IX_7 , namely, $\text{IO}_3(\text{OH})$, $\text{IO}_2(\text{OH})_3$, and $\text{IO}(\text{OH})_5$, and the last are types of diperiodic salts, which correspond with the type of the meso-salts, in the same way as pyrophosphoric salts correspond with orthophosphoric salts—i.e., $2\text{H}_3\text{IO}_5 - \text{H}_2\text{O} = \text{H}_4\text{I}_2\text{O}_9$.

⁸⁵ Periodic acid, which was discovered by Magnus and Ammermüller, and the salts of which were afterwards studied by Langlois, Rammelsberg, and many others, presents examples of hydrates in which it is evident that there is not that distinction between the water of hydration and of crystallisation which was at first considered to be so clear. In $\text{HClO}_4, 2\text{H}_2\text{O}$, the water, $2\text{H}_2\text{O}$, is not displaced by bases, and must be regarded as water of crystallisation, whilst in $\text{HIO}_4, 2\text{H}_2\text{O}$ it must be regarded as water of hydration. We shall afterwards see that the system of the elements obliges us to consider the halogens as substances giving a highest saline type, GX_7 , when G signifies a halogen, and X oxygen ($\text{O}=\text{X}_2$), OH, and other like elements.

⁸⁶ With respect to hydrogen, oxygen, chlorine, and other elements, bromine occupies an intermediate position between chlorine and iodine, and there is therefore no particular need for considering at length the compounds of bromine. This is the great advantage of a natural grouping of the elements.

⁸⁷ They were both obtained by Gay-Lussac and many others. Recent data respecting iodine monochloride, ICl , entirely confirm the numerous observations of Trapp (1854), and even confirm his statement as to the existence of two isomeric (liquid and crystalline) forms (Stortenbeker). With a small excess of iodine, iodine monochloride remains liquid, but in the presence of traces of iodine trichloride it easily crystallises. Tanatar (1893) showed that of the two modifications of ICl , one is stable, and melts at 27° ; while the other, which easily passes into the first, and is formed in the absence of ICl_3 , melts at 14° . Schützenberger amplified the data concerning the action of water on these chlorides (note 88), and Christomanos gave the fullest data regarding the trichloride.

Stortenbeker (1888) investigated the equilibrium of the system containing the molecules I_2 , ICl , ICl_3 , and Cl_2 , in the same way that Roozeboom (Chap. X., note 38) examined the equilibrium of the molecules HCl , $\text{HCl}, 2\text{H}_2\text{O}$, and H_2O . He found that iodine monochloride appears in two states: one (the ordinary) is stable and melts at 27.2° , while the other is obtained by rapid cooling, and melts at 13.9° , and easily passes into the first form. Iodine trichloride melts at 101° only in a closed tube under a pressure of 16 atmospheres.

from dry iodine and chlorine.⁸⁸ Both substances are formed in a number of reactions; for example, by the action of aqua regia on iodine, of chlorine on hydriodic acid, of hydrochloric acid on periodic acid, of iodine on potassium chlorate (with the aid of heat, &c.). Trapp obtained iodine monochloride, in beautiful red crystals, by passing a rapid current of chlorine into molten iodine. The monochloride then distils over and solidifies, melting at 27°. By passing chlorine over the crystals of the monochloride, it is easy to obtain iodine trichloride in orange crystals, which melt at 34° and volatilise at 47°, but in so doing decompose (into Cl₂ and ClI). The chemical properties of these chlorides entirely resemble those of chlorine and iodine, as would be expected, because, in this instance, a combination of similar substances has taken place, just as in the formation of solutions or alloys. Thus, for instance, the unsaturated hydrocarbons (for example, C₂H₄), which are capable of directly combining with chlorine and iodine, also directly combine with iodine monochloride.

⁸⁸ By the action of water on iodine monochloride and trichloride a compound IHCl₂ is obtained, which does not seem to be altered by water. Besides this compound, iodine and iodic acid are always formed, $10\text{ICl} + 3\text{H}_2\text{O} = \text{HIO}_3 + 5\text{IHCl}_2 + 2\text{I}_2$.

CHAPTER XII

SODIUM

Sodium sulphate Na_2SO_4 , obtained when a mixture of sulphuric acid and common salt is strongly heated (Chapter X.),¹ forms a colourless saline mass consisting of fine crystals, soluble in water. It is the product of many other double decompositions, sometimes carried out on a large scale; for example, when ammonium sulphate is heated with common salt, in which case the sal-ammoniac is volatilised, also by the action of cold upon a mixture of strong solutions of sulphate of magnesium and sodium chloride, &c. A similar reaction also takes place when, for instance, a mixture of lead sulphate and common salt is heated; this mixture readily fuses, and if the temperature is further raised heavy vapours of lead chloride appear. When the disengagement of these vapours ceases, the remaining mass, on being treated with water, yields a solution of sodium sulphate mixed with a solution of undecomposed common salt. A portion of the lead sulphate remains unchanged. The cause and nature of the reaction are just the same as those indicated when considering the action of sulphuric acid on NaCl . Here too it may be shown that the double decomposition is determined by the removal of PbCl_2 from the sphere of action of the remaining substances. This is seen from the fact that sodium sulphate, on being dissolved in water and mixed with a solution of any lead salt (and even with a solution of lead chloride, although this latter is but sparingly soluble in water), gives a white precipitate of lead sulphate. The reaction in the solution depends upon the insolubility of the lead sulphate, and the decomposition which takes place on heating is due to the volatility of the lead chloride. Silver sulphate, Ag_2SO_4 , in solution with common salt, gives silver chloride, because the latter

¹ While describing in some detail the properties of sodium chloride, hydrochloric acid, &c., I wish to impart, by separate examples, an idea of the properties of saline substances, but the dimensions of this work and its purpose and aim do not permit of entering into particulars concerning every salt, acid, or other substance. The fundamental object of this work—an account of the characteristics of the elements and an acquaintance with the forces acting between atoms—would not be attained by the multiplication of the number of as yet ungeneralised properties and relations, but they extend our horizon and excite a spirit of inquiry.

is insoluble in water, $\text{Ag}_2\text{SO}_4 + 2\text{NaCl} = \text{Na}_2\text{SO}_4 + 2\text{AgCl}$. Sodium carbonate, mixed in solution with the sulphates of iron, copper, manganese, magnesium, &c., gives in solution sodium sulphate, and in the precipitate a carbonate of the corresponding metal, because these salts of carbonic acid are insoluble in water; for instance, $\text{MgSO}_4 + \text{Na}_2\text{CO}_3 = \text{Na}_2\text{SO}_4 + \text{MgCO}_3$. In precisely the same way sodium hydroxide acts on solutions of the majority of the salts of sulphuric acid, containing metals the hydroxides of which are insoluble in water—for instance, $\text{CuSO}_4 + 2\text{NaHO} = \text{Cu}(\text{HO})_2 + \text{Na}_2\text{SO}_4$.²

Thus where sulphates and salts of sodium are in contact, it may be expected that sodium sulphate will be formed and separated if the conditions are favourable; for this reason it is not surprising that sodium sulphate is often found in the native state. Some of the springs and salt lakes in the steppes beyond the Volga, and in the Caucasus, contain a considerable quantity of sodium sulphate, and yield it by simple evaporation of the solutions. Beds of this salt are also met with; thus at a depth of only 5 feet, about 38 versts to the east of Tiflis, at the foot of the range of the 'Wolf's mane' (*Voltchia griva*) mountains, a deep stratum of very pure Glauber's salt, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, has been found.³ A layer two metres thick of the same salt lies at the bottom of several lakes (an area of about 10 square kilometres) in the Kouban district near Batalpaschinsk, and here its working was begun in 1887. In Spain, near Aranjuez and in many parts of the Western States of North America, mineral sodium sulphate has likewise been found, and is already being worked. In the Karabougask Bay, which is cut off from the Caspian Sea by sandbanks, the sea water is concentrated by evaporation, and deposits Glauber's salt under the action of cold.

The methods of obtaining salts by means of double decomposition from others already prepared are so general that in describing a given salt there is no necessity to enumerate the cases hitherto observed of its being formed through various double decompositions. The possibility of this occurrence ought to be foreseen, according to Berthollet's

² Anhydrous (ignited) sodium sulphate, Na_2SO_4 , is known in trade as 'sulphate' or salt-cake, and in mineralogy as *thénardite*. The crystalline decahydrated salt is termed in mineralogy *mirabilite*, and in trade Glauber's salt. On fusing it, the monohydrate, $\text{Na}_2\text{SO}_4 \cdot \text{H}_2\text{O}$, is obtained, together with a supersaturated solution.

³ The salts may be obtained, not only by methods of substitution of various kinds, but also by many other combinations. Thus sodium sulphate may be formed from sodium oxide and sulphuric anhydride, by oxidising sodium sulphide, Na_2S , or sodium sulphite, Na_2SO_3 , &c. When sodium chloride is heated in a mixture of the vapours of water, air, and sulphurous anhydride, sodium sulphate is formed. According to this method, sodium sulphate, Na_2SO_4 , is obtained from NaCl without the preliminary manufacture of H_2SO_4 . Lumps of NaCl pressed into the form of bricks are loosely packed into a cylinder and subjected, above 400° , to the action of steam, air, and SO_2 . Under these conditions, HCl , sulphate, and a certain amount of unaltered NaCl are obtained.

doctrine, from the properties of the salt in question. On this account it is most important to know the properties of salts; all the more so because up to the present time those very properties (solubility, formation of definite crystallo-hydrates, &c.) which may be made use of for separating them from other salts have not been generalised.⁴ These properties yet remain subjects for investigation, and are rarely—by analogy only—to be foreseen.⁵

Sulphate of sodium, Na_2SO_4 (it fuses at 843°), is soluble in water at all temperatures, but it separates out from its solutions in an anhydrous form only at temperatures above 32.5° , and then the solubility of the salt falls as the temperature rises, so that a saturated solution, when heated, deposits a portion of the salt, this being for 100 grams of water :

At	40°	50°	100°	230°	320°
Na_2SO_4	48.8	46.7	42.5	43.9	21.7 grams

⁴ Given a salt MX, formed by metal M and haloid X, it is possible to predict many of its reactions with great certainty without having recourse to experiment, but only on the strength of analogy and of the general laws governing the course of chemical change. But the solubility of the salt in water and other liquids, its faculty for giving one or another crystallo-hydrate, and their solubility and mode of transformation into each other, cannot yet be foreseen, because this subject has been methodically investigated in only a few cases, and then chiefly owing to the interest provoked by Gibbs's 'theory of phases' (see Chap. XXIV., note 9a), and the researches of van't Hoff, Bakhuis Roozeboom, Meyerhoffer, and others, on equilibrium (see Chap. XI., note 9; Chap. XIV., note 50; Chap. XXII., note 23, &c.). Although recognising the great utility of the present tendency of this subject in facilitating the generalisation of scientific observations and in preparing the way for a true theory, I limit myself in this work to fragmentary information on this complicated subject, because I consider that as yet it should only be studied after an acquaintance with the principles of chemistry has been acquired—all the more so because in text-books of physical chemistry the question is as yet chiefly concerned with the expression of phenomena and not with their prediction; as is seen, for instance, from the fact that the cause of the profound difference between a rise in solubility with the temperature for some substances and a fall for others yet remains entirely unknown. So long as this fall formed an isolated phenomenon (for Na_2SO_4 at first) it might be accepted, with the help of certain concessions, but now it is known to occur with the majority of the sulphates (see, for instance, Chap. I., note 23a, CaSO_4 , the sulphates of Ce, La, Di, Th, &c.; Étard, Muthmann, and others), and it is evident that this fall in the solubility (with a rise of temperature) is a very common phenomenon, the explanation of which can hardly be expected by simply applying the 'theory of phases,' but which must be taken into consideration for explaining the nature of solutions in order to comprehend the relations and forces acting in the formation of solutions and crystallo-hydrates. In my opinion no right issue is possible without recognising the agency of a chemism (special attraction or affinity) in the matter, and the 'theory of phases' only explains and describes the physico-chemical aspect of the subject.

⁵ The data given for the solubility of Na_2SO_4 at temperatures below 100° are taken almost exclusively from the old works of Gay-Lussac, and partly (for the heptahydrated salt) from Levelle, because, among the more recent determinations, I have found none either fuller or indicating the existence of any important errors in the former data. I think that in such an historical instance as Na_2SO_4 it would be most desirable to have fresh, full, and exact data for the solubility at different temperatures.

The data for temperatures above 100° were obtained (Étard, 1892) in sealed vessels under the pressure of the vapour,⁶ and show that the solubility varies little between 100° and 230° ,⁷ but that it falls rapidly between 32.5° and 100° , and also above 230° . Under ordinary conditions the crystallo-hydrate of the composition $\text{Na}_2\text{SO}_4, 10\text{H}_2\text{O}$ separates out at all temperatures below 32.5° . It is known as Glauber's salt, and contains 78.9 grams of anhydrous salt per 100 grams of water. At these temperatures the anhydrous salt is entirely converted into the decahydrated salt, or dissolves in the presence of water.⁸ The strength (concentration) corresponding to the decahydrated salt (73 per cent.) is never attained by solutions under any conditions of temperature, and if

⁶ Perhaps this increase of pressure participates in the phenomenon, and therefore it would be desirable to have determinations of the solubility of Na_2SO_4 at temperatures above 100° under different pressures. I may mention that a fall of solubility, with a rise of temperature, is known for many salts (Chap. I., note 24), and that Étard considers the composition, $\text{Na}_2\text{SO}_4, 18\text{H}_2\text{O}$, to be constant for saturated solutions between 100° and 230° .

⁷ Tilden (1884) gives the following data: at 100° , 43 parts of salt per 100 of water; at 140° , 42 parts; at 160° , 43 parts; at 180° , 44 parts, and at 230° , 46 parts. The discrepancy between these and Étard's figures can only be removed by fresh determinations. This is all the more desirable as it concerns the question of solutions and such a classical example as Glauber's salt. It is evident that beyond analysis, i.e., determining the composition of saturated solutions, the variation of volumes and densities, the influence of pressure, the presence or absence of an excess of salt (solid *phase*), separation of salt by alcohol, supersaturation, vapour pressures of solutions and hydrates, &c., must also be investigated in this case. Wyrouboff (1890) showed that the anhydrous salt occurs in two dimorphous states, one of which is unstable and the other stable; the crystals of the former evince a strong double refraction, while those of the latter are almost isotropic. The former occurs in nature under the name of *thénardite*, and the latter is completely obtained either after fusing or heating to 200° the first modification. By evaporating solutions of Na_2SO_4 at temperatures above 40° Wyrouboff obtained a mixture of both modifications, in which the proportion of the second variety increased with the temperature, so that at 100° only a very small amount of the unstable variety remained in the mixture. Wyrouboff endeavours to explain the anomalies observed in the solubility of Na_2SO_4 above 32.5° by these variations; and although there are not yet sufficient grounds for accepting these views, still the fact of this dimorphism should be taken into consideration in investigating the solubility of Na_2SO_4 . It may be mentioned that the sp. gr. of Na_2SO_4 is 2.66; that of $\text{Na}_2\text{SO}_4, 10\text{H}_2\text{O}$, 1.46; and that of solutions containing p per cent. of the anhydrous salt at $15^{\circ}/4^{\circ}$, $9,992 + 90.2p + 0.35p^2$ if the sp. gr. of water at 4° be taken as 10,000. It follows from these figures that the solutions are formed from water and salt (hydrated or anhydrous) with a contraction of volume, that is, that an increase of volume takes place when the salt separates out.

⁸ Direct experiment made by the author showed that if a saturated solution of Na_2SO_4 be taken at the ordinary temperature, and some anhydrous salt be added to it, a portion of the salt will crystallise out from the solution, part of the water being used up in converting the anhydrous into the decahydrated salt; so that if the residue be collected and dried it will be found to contain more anhydrous salt than was added to the solution. If the anhydrous salt is rinsed with water below 32.5° , in insufficient quantity to dissolve the salt, the first portions of water are consumed in crystallising the salt, and solution is only accomplished by an excess of water. Thus, anhydrous salt + water = decahydrated salt + solution. This is a form of distribution. The anhydrous salt hardens like gypsum if a small quantity of a saturated solution is poured over it.

the crystals which separate out are heated, although they melt at a constant temperature of 32.484° ,⁹ yet they immediately deposit a portion of the salt in an anhydrous form, so that the temperature 32.5° must be regarded as being the limiting or *transition* temperature, above which the decahydrated salt cannot exist, and below which its solutions do not give the anhydrous salt. The solubility between 0° and this transition temperature is the same, no matter whether the anhydrous or the decahydrated salt be taken, 100 grams of water dissolving :

At	0°	10°	20°	30°
Na_2SO_4	5.0	9.0	19.4	40.0 grams
$\text{Na}_2\text{SO}_4, 10\text{H}_2\text{O}$	12.1	23.0	58.3	183.9 ,,

The solubility at the transition temperature, 32.5° , reaches 55 grams (according to Levallois and others 52.7 grams, or even 50.65 grams) of Na_2SO_4 per 100 grams of water, and if such a saturated solution (or one nearly so) be poured off from the excess of salt, or, better still, if a solution saturated at a higher temperature be cooled without access of air (which might contain crystals of the decahydrated salt, which would evoke crystallisation), then no salt will separate out, and a *supersaturated* solution will be obtained containing more salt than that given above for low temperatures. If such a solution is cooled to between $+5^{\circ}$ and $+7^{\circ}$, it deposits crystals of a heptahydrated salt, $\text{Na}_2\text{SO}_4, 7\text{H}_2\text{O}$, which is far more soluble than the decahydrated salt, 100 grams of water dissolving, according to Levelle :

At	0°	10°	20°	26°
Na_2SO_4	19.6	30.5	44.7	55.0 grams.
$\text{Na}_2\text{SO}_4, 7\text{H}_2\text{O}$	44.8	78.9	140.0	202.6 grams.

It is evident that a saturated solution of the heptahydrated salt will be supersaturated for the decahydrated salt, and therefore the smallest trace of the latter will evoke the crystallisation of the supersaturated solution with the formation of the decahydrated salt and evolution of heat.^{9a} No separation of salt is caused by the introduction of a trace

⁹ Richards gave this figure (according to the mercurial thermometer), and observed the extreme constancy of this temperature, and therefore proposed employing it for verifying thermometers, more especially as large quantities of $\text{Na}_2\text{SO}_4, 10\text{H}_2\text{O}$ may be prepared with great ease.

^{9a} As heat is absorbed during the solution of the salt, it is evolved when the salt crystallises out from solution. According to Pickering's experiments (1886), the molecular weight in grams (that is, 142 grams) of anhydrous sodium sulphate, on being dissolved in a large mass of water, at 0° absorbs (hence the — sign) $-1,100$ heat units; at 10° , -700 ; and at 20° (gives out), $+25$. For the salt, $\text{Na}_2\text{SO}_4, 10\text{H}_2\text{O}$, at 10° , $-4,000$; and at 20° , $-3,160$. Hence it is evident that the decahydrated salt dissolving in water gives a decrease of temperature. Solutions in hydrochloric acid give a still greater decrease, probably because a certain quantity of sodium chloride is formed.

of the solid anhydrous or heptahydrated salt into the solution.¹⁰ The addition of alcohol, in which all sulphates are only slightly soluble, to the supersaturated solution, leads to the separation of the heptahydrated salt. The latter is only formed from solutions below 27°. Separate crystals of this salt, at this and higher temperatures, become opaque, and already contain a mixture of the anhydrous and decahydrated salt. This clearly shows the instability of the equilibrium which exists in this salt (see Chap. XIV., note 50).

Both the deca- and hepta-hydrated salts effloresce and readily lose water, even at the ordinary temperature.

Sodium sulphate, Na_2SO_4 , only enters into a few reactions of combination with other salts, and chiefly with salts of the same acid, forming double sulphates. Thus, for example, if a solution of sodium sulphate is mixed with a solution of aluminium, magnesium, or ferrous sulphate, it gives crystals of a double salt when evaporated. Sulphuric acid itself forms with sodium sulphate a compound like these double salts. It is formed with great ease when sodium sulphate is dissolved in sulphuric acid and the solution evaporated. On evaporation, crystals of the **acid salt** separate, $\text{Na}_2\text{SO}_4 + \text{H}_2\text{SO}_4 = 2\text{NaHSO}_4$. This separates from hot solutions, while the crystallo-hydrate, $\text{NaHSO}_4, \text{H}_2\text{O}$,^{10a} separates from cold solutions. The crystals, when exposed to damp air, decompose into H_2SO_4 , which deliquesces, and Na_2SO_4 (Graham, Rose); alcohol also extracts sulphuric acid from the acid salt. This shows the feeble force which holds the sulphuric acid to the sodium sulphate.¹¹ Both acid sodium sulphate and all mixtures of the normal salt and sulphuric acid lose water when heated, and are converted into sodium **pyrosulphate**, $\text{Na}_2\text{S}_2\text{O}_7$, at a low red heat.^{11a} This anhydrous

¹⁰ The anhydrous salt must be calcined for this purpose. If it be obtained by the efflorescence of the hydrated salts, it can, according to Gernez, lead to the formation of crystals of the heptahydrated salt. If much of the anhydrous salt is taken it hardens, as mentioned in note 8.

^{10a} The very large and well-formed crystals of this salt resemble the hydrate $\text{H}_2\text{SO}_4, \text{H}_2\text{O}$, or $\text{SO}(\text{OH})_4$. In general the replacement of hydrogen by sodium modifies many of the properties of acids less than its replacement by other metals. This most probably depends on the volumes being nearly equal.

¹¹ In solution (Berthelot) the acid salt in all probability decomposes most in the greatest mass of water. The specific gravity (according to the determinations of Marignac) of solutions at 15°/4° is given by $9,992 + 77.92p + 0.231p^2$. From these figures, and from the specific gravities of sulphuric acid, it is evident that, on mixing solutions of this acid and sodium sulphate, *expansion* will always take place; for instance, $\text{H}_2\text{SO}_4 + 25\text{H}_2\text{O}$ with $\text{Na}_2\text{SO}_4 + 25\text{H}_2\text{O}$ increases from 483 volumes to 486. In addition to which, in weak solutions heat is absorbed, as shown in Chap. X., note 27. Nevertheless, even more acid salts may be formed and obtained in a crystalline form. For instance, on cooling a solution of 1 part of sodium sulphate in 7 parts of sulphuric acid, crystals of the composition $\text{NaHSO}_4, \text{H}_2\text{SO}_4$ are separated (Schultz, 1868). This compound fuses at about 100°, and the ordinary acid salt, NaHSO_4 , at 149°.

^{11a} On decreasing the pressure, sodium hydrogen sulphate, NaHSO_4 , dissociates

salt, at a bright red heat, parts with the elements of sulphuric anhydride, the normal sodium sulphate remaining behind: $\text{Na}_2\text{S}_2\text{O}_7 = \text{Na}_2\text{SO}_4 + \text{SO}_3$.

Sodium sulphate may by double decomposition be converted into a sodium salt of any other acid, by means of heat—taking advantage of the volatility—or by means of solution—taking advantage of the different degrees of solubility of the different salts. Thus, for instance, owing to the insolubility of barium sulphate, sodium hydroxide or caustic soda may be prepared from sodium sulphate, if barium hydroxide be added to its solution, $\text{Na}_2\text{SO}_4 + \text{Ba}(\text{HO})_2 = \text{BaSO}_4 + 2\text{NaHO}$. And by taking any salt of barium, BaX_2 , the corresponding salt of sodium may be obtained, $\text{Na}_2\text{SO}_4 + \text{BaX}_2 = \text{BaSO}_4 + 2\text{NaX}$. Barium sulphate, being a very sparingly soluble salt, is obtained in this way as a precipitate, whilst the sodium hydroxide, or salt, NaX , is obtained in solution, because **nearly all salts of sodium are soluble**. The doctrine of double saline decompositions permits all such cases to be foreseen.

Sodium sulphate by itself is very stable, and it is only at a temperature sufficient to melt iron that it gives up the elements SO_3 , and then only partially. However, the oxygen may be separated from sodium sulphate, as from all other sulphates, by means of many substances, such as charcoal and sulphur, but hydrogen is not able to produce this reducing action. If sodium sulphate be heated with charcoal, then carbonic oxide and anhydride are evolved, and there is produced, according to the conditions, either the lower oxygen compound, sodium sulphite, Na_2SO_3 (for instance, in the formation of glass); or else the decomposition proceeds further, and sodium sulphide, Na_2S , is formed, according to the equation, $\text{Na}_2\text{SO}_4 + 2\text{C} = 2\text{CO}_2 + \text{Na}_2\text{S}$.

On the basis of this reaction the sulphate of sodium prepared at chemical works is converted into **soda ash**—that is, **sodium carbonate**, Na_2CO_3 , which is used for many purposes. In the form of carbonates, the metallic oxides behave in many cases just as they do in the state of oxides or hydroxides, owing to the feeble acid properties of carbonic acid. However, the majority of the salts of carbonic acid are insoluble, whilst sodium carbonate is one of the few soluble salts of this acid and therefore reacts with facility. Hence sodium carbonate is employed for many purposes, in which its alkaline properties come into play. Thus, even under the action of feeble organic acids it immediately parts with its carbonic acid, and gives a sodium salt of the acid taken. Its solutions exhibit an alkaline reaction on litmus. It aids the passage of certain organic substances (tar, acids) into solution, and is therefore

much more easily than at the ordinary pressure; it loses water and forms the pyro-sulphate, $\text{Na}_2\text{S}_2\text{O}_7$; this reaction is utilised in chemical works.

used, like caustic alkalies and soap (which latter also acts by virtue of the alkali it contains), for the removal of certain organic substances, especially in bleaching cotton and similar fabrics. Besides which a considerable quantity of sodium carbonate is used for the preparation of sodium hydroxide or caustic soda, which has also a very wide application. In large chemical works where sodium carbonate is manufactured from Na_2SO_4 , it is usual first to manufacture sulphuric acid, and then by its aid to convert common salt into sodium sulphate, and lastly to convert the sodium sulphate thus obtained into carbonate and caustic soda. Hence these works prepare both alkaline substances (soda ash and caustic soda) and acid substances (sulphuric and hydrochloric acids), the two classes of chemical products which are distinguished for the greatest energy of their reactions, and are therefore most frequently applied to technical purposes. Factories manufacturing soda in this manner are generally called alkali works.

The process of the conversion of sodium sulphate into sodium carbonate consists in strongly heating a mixture of the sulphate with charcoal and calcium carbonate. The following reactions then take place: the sodium sulphate is first deoxidised by the charcoal, forming sodium sulphide and carbonic anhydride, $\text{Na}_2\text{SO}_4 + 2\text{C} = \text{Na}_2\text{S} + 2\text{CO}_2$. The sodium sulphide thus formed then enters into double decomposition with the calcium carbonate taken, and gives calcium sulphide, CaS , and sodium carbonate, $\text{Na}_2\text{S} + \text{CaCO}_3 = \text{Na}_2\text{CO}_3 + \text{CaS}$.

Besides which, under the action of the heat, a portion of the excess of calcium carbonate is decomposed into lime and carbonic anhydride, $\text{CaCO}_3 = \text{CaO} + \text{CO}_2$, and the carbonic anhydride with the excess of charcoal forms carbon monoxide, which towards the end of the operation shows itself by the appearance of a blue flame. Thus from a mass containing sodium sulphate we obtain a mass which includes sodium carbonate, calcium sulphide, and calcium oxide, but none of the sodium sulphide formed on first heating the mixture. The entire process, which proceeds at a high temperature, may be expressed by a combination of the three above-mentioned equations, if it be considered that the product contains one equivalent of calcium oxide to two equivalents of calcium sulphide.¹² The sum of the reactions may then be expressed

¹² Calcium sulphide, CaS , like many metallic sulphides which are soluble in water, is decomposed by it (Chap. X.), $\text{CaS} + \text{H}_2\text{O} = \text{CaO} + \text{H}_2\text{S}$, because hydrogen sulphide is a very feeble acid. If calcium sulphide be acted on by a large mass of water, lime may be precipitated, and a state of equilibrium will be reached when the system $\text{CaO} + 2\text{CaS}$ remains unchanged by water. Lime, being a product of the action of water on CaS , limits this action. Therefore, if in black ash the lime were not in excess, a part of the sulphide would be in solution. In this manner, in the manufacture of sodium carbonate the conditions of equilibrium which enter into double decompositions have been made use of (see above), and the aim is to form directly the unchangeable product, $\text{CaO}, 2\text{CaS}$.

thus: $2\text{Na}_2\text{SO}_4 + 3\text{CaCO}_3 + 9\text{C} = 2\text{Na}_2\text{CO}_3 + \text{CaO}, 2\text{CaS} + 10\text{CO}$. Indeed, the quantities in which the substances are mixed together at chemical works approach the proportions required by this equation. The entire process of decomposition is carried on in reverberatory furnaces, into which a mixture of 1,000 parts of sodium sulphate, 1,040 parts of calcium carbonate (as a somewhat porous limestone), and 500 parts of small coal is introduced from above. This mixture is first heated in the portion of the furnace which is furthest removed from the fire-grate; it is then brought to the part nearest the fire-grate, when it is stirred during heating. The partially fused mass obtained at

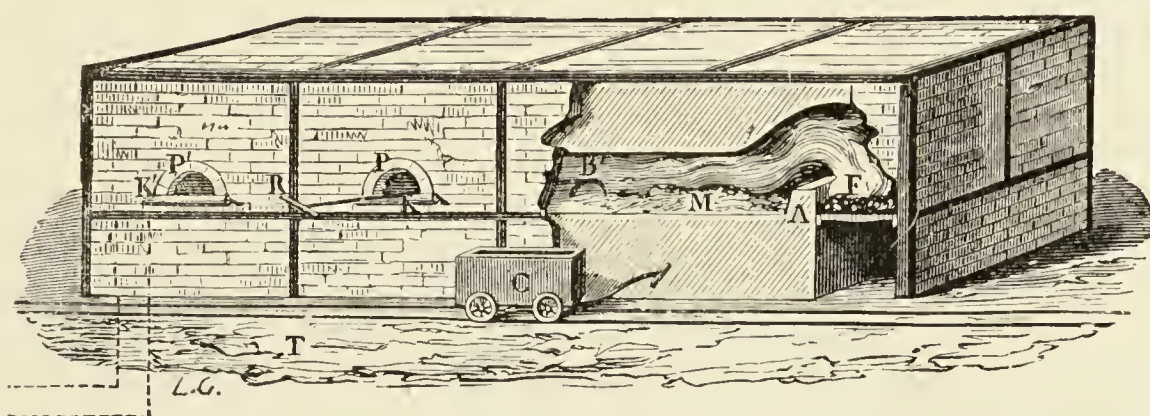


FIG. 78.—Reverberatory furnace for the manufacture of sodium carbonate. F, the grate, A, the bridge, M, the hearth for the ultimate calcination of the mixture of sodium sulphate, coal, and calcium carbonate, which is charged from above into the part of the furnace furthest removed from the fire F. P, P, doors for stirring and bringing the mass towards the grate F by means of stirrers R. At the end of the operation the semi-fused mass is charged into trucks C.

the end of the process is cooled, and then subjected to methodical lixiviation¹³ to extract the sodium carbonate, the mixture of calcium

This was first regarded as a special insoluble compound, but there is no evidence of its independent existence.

¹³ **Methodical lixiviation** is the extraction, by means of water, of a soluble substance from the mass containing it. It is carried on so as not to obtain weak aqueous solutions, and in such a way that the residue shall not contain any of the soluble substance. This problem is of great practical importance in many industries. It is required to extract from the mass all that is soluble in water. This is easily effected if water is first poured on the mass, the strong solution thus obtained decanted, then water again poured on, time being allowed for it to act, then again decanted, and so on until fresh water does not take up anything. But then such weak solutions are finally obtained that it would be very disadvantageous to evaporate them. This is avoided by pouring the fresh hot water destined for the lixiviation, not on to the fresh mass, but upon a mass which has already been subjected to a first lixiviation by weak solutions. In this way the fresh water gives a weak solution. The strong solution which goes to the evaporating pan flows from those parts of the apparatus which contain the fresh, as yet unlixivated, mass, and thus in the latter parts the weak alkali formed in the other parts of the apparatus becomes saturated as far as possible with the soluble substance. Generally several intercommunicating vessels (standing at the same level) are constructed, into which the fresh mass which is intended for lixiviation is charged in turn; the water is poured in, the alkali drawn off, and the lixiviated residue removed. The illustration represents such an apparatus, consisting of four communicating vessels. The water poured into one of them flows through the two nearest and issues from the third. The fresh mass being placed in one of these boxes or vessels, the stream of water passing

oxide and sulphide forming the so-called 'soda waste' or 'alkali waste.'¹⁴

through the apparatus is directed in such a manner as to finally issue from this vessel containing the fresh unlixivated mass. The fresh water is added to the vessel containing the material which has been almost completely exhausted. Passing through this vessel it is conveyed by the pipe (syphon passing from the bottom of the first box to the top of the second) communicating with the second; it finally passes (also through a syphon pipe) into the box (the third) containing the fresh material. The water will extract all that is soluble in the first vessel, leaving only an insoluble residue. This vessel is then ready to be emptied, and refilled with fresh material. The levels of the liquids in the various vessels will naturally be different, in consequence of the various strengths of the solutions which they contain.

Sodium carbonate does not pass into solution alone; there is also some caustic soda with it, formed by the action of lime on the carbonate of sodium, and also sodium

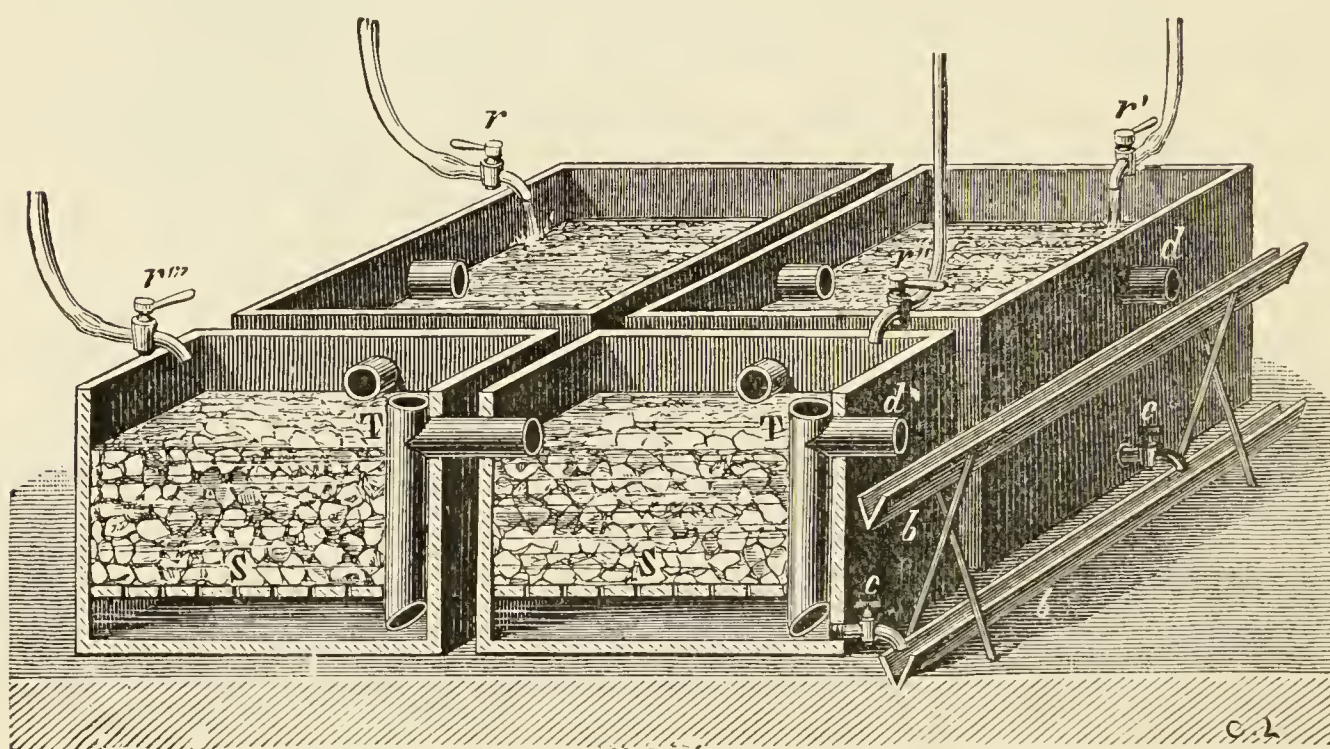


FIG. 79.—Apparatus for the methodical lixiviation of black ash, &c. Water flows into the tanks from the pipes, *r*, *r'*, and the saturated liquid is drawn off from *c*, *c*.

sulphide and certain other compounds. The sodium carbonate solution therefore is not obtained in a very pure state. The solution is concentrated by evaporation, which is conducted by means of the waste heat from the soda furnaces, together with that of the gases given off.

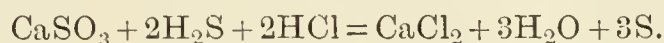
Part of the sodium carbonate is recrystallised in order to purify it more thoroughly. In order to do this a saturated solution is left to crystallise, at a temperature below 30°, in a current of air, in order to promote the separation of the water vapour. The large transparent crystals (efflorescent in air) of $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, which have already been spoken of (Chap. I.), are then formed.

¹⁴ The whole of the sulphur used in the production of the sulphuric acid employed in decomposing the common salt is contained in this residue. This is the great burden and expense of the soda works which use Leblanc's method. As an instructive example from a chemical point of view, it is worth while mentioning here two of the various methods of recovering the sulphur from the soda waste. Chance's process is treated in Chap. XX., note 6.

Kynaston (1885) treats the soda waste with a solution (sp. gr. 1.21) of magnesium chloride, which disengages sulphuretted hydrogen: $\text{CaS} + \text{MgCl}_2 + 2\text{H}_2\text{O} = \text{CaCl}_2 + \text{Mg}(\text{OH})_2 + \text{H}_2\text{S}$. Sulphurous anhydride is passed through the residue in order to form

The above-mentioned method for making soda was discovered in the year 1808 by the French doctor *Leblanc*, and is known as the **Leblanc process**. The particulars of the discovery are somewhat remarkable. Sodium carbonate, having a considerable application in industry, was for a long time prepared exclusively from the ash of marine plants (Chap. XI., on iodine). Even up to the present time this process is carried on in Normandy. In France, where for a long time the manufacture of large quantities of soap (so-called Marseilles soap) and various fabrics required a large amount of soda, the quantity prepared at the coast was insufficient to meet the demand. For this reason, during the wars at the beginning of the last century, when the import of foreign goods into France was interdicted, the want of sodium carbonate was felt. The French Academy offered a prize for the discovery of a profitable method of preparing it from common salt. Leblanc then proposed the above-mentioned process, which is remarkable for its great simplicity.¹⁵

the insoluble calcium sulphite: $\text{CaCl}_2 + \text{Mg}(\text{OH})_2 + \text{SO}_2 = \text{CaSO}_3 + \text{MgCl}_2 + \text{H}_2\text{O}$. The solution of magnesium chloride obtained is again used, and the washed calcium sulphite brought into contact at a low temperature with hydrochloric acid (a weak aqueous solution) and hydrogen sulphide, the whole of the sulphur then separating:



But most efforts have been directed towards avoiding the formation of soda waste, that is, to obtaining soda from NaCl without converting it into Na_2SO_4 , and consequently without manufacturing H_2SO_4 , as will be presently described.

¹⁵ Among the drawbacks of the Leblanc process are (1) the accumulation of 'soda waste' (note 14) owing to the impossibility, at the comparatively low price of sulphur (especially in the form of pyrites), of finding uses for the sulphur and sulphur compounds for which this waste is sometimes treated, and (2) the insufficient purity of the sodium carbonate for many purposes. The advantages of the Leblanc process, besides its simplicity and cheapness, are that almost the whole of the acids obtained as by-products have a commercial value; for chlorine and bleaching powder are produced from the large amount of hydrochloric acid which appears as a by-product; caustic soda also is very easily made, and the demand for it increases every year.

As an example of the other numerous and varied methods of manufacturing soda from sodium chloride, the following may be mentioned: Sodium chloride is decomposed by oxide of lead, PbO , forming lead chloride and sodium oxide, which, with carbonic anhydride, yields sodium carbonate (Scheele's process). In Cornu's method, sodium chloride is treated with lime, and then exposed to the air, when it yields a small quantity of sodium carbonate. In E. Kopp's process, sodium sulphate (125 parts) is mixed with oxide of iron (80 parts) and charcoal (55 parts), and the mixture heated in reverberatory furnaces. Here a compound, $\text{Na}_6\text{Fe}_4\text{S}_3$, is formed, which is insoluble in water, absorbs oxygen and carbonic anhydride, and then forms sodium carbonate and ferrous sulphide; when roasted this gives sulphurous anhydride, the indispensable material for the manufacture of sulphuric acid, and ferric oxide, which is again used in the process. Gossage prepares Na_2S from Na_2SO_4 (by heating it with carbon), dissolves it in water and subjects the solution to the action of an excess of CO_2 in coke towers, thus obtaining H_2S (a gas which gives SO_2 under perfect combustion, or sulphur when incompletely burnt) and bicarbonate of sodium; $\text{Na}_2\text{S} + 2\text{CO}_2 + 2\text{H}_2\text{O} = \text{H}_2\text{S} + 2\text{HNaCO}_3$. The latter gives soda and CO_2 when ignited. This process should, in my opinion, be

Of the other industrial processes for manufacturing sodium carbonate, the **ammonia process** is the most worthy of mention.¹⁶ In this the vapours of ammonia, and then an excess of carbonic anhydride, are directly introduced into a concentrated solution of sodium chloride in order to form the acid ammonium carbonate, NH_4HCO_3 . Then, by means of the double saline decomposition of this salt, sodium chloride is decomposed, and in virtue of its slight solubility acid sodium carbonate, NaHCO_3 , is precipitated and ammonium chloride, NH_4Cl , obtained in solution (with a portion of the sodium chloride and acid sodium carbonate). The reaction proceeds in the solution, owing to the sparing solubility of the NaHCO_3 , according to the equation: $\text{NaCl} + \text{NH}_4\text{HCO}_3 = \text{NH}_4\text{Cl} + \text{NaHCO}_3$. The ammonia is recovered from the solution by heating it with lime or magnesia,^{16a} and the precipitated acid sodium carbonate is converted into the normal salt by heating. It is thus obtained in a very pure state and cheaper, because the NH_3 can be almost all recovered, there is no soda waste, and the preliminary manufacture of a large quantity of sulphuric acid is unnecessary.¹⁷

suitable for the treatment of native Na_2SO_4 , like that which is found in the Caucasus, all the more so because H_2S gives sulphur as a by-product.

In recent times soda (and chlorine, see Chap. II., note 1) is prepared from strong solutions of salt by the action of an electric current, but this method in reality gives NaHO and not soda. According to Hempel (1890) soda in crystals is deposited when an electric current and a stream of carbonic acid gas are passed through a saturated solution of NaCl .

Sodium carbonate may likewise be obtained from cryolite (Chap. XVII., note 23), the method of treating which will be mentioned under Aluminium.

¹⁶ This process (Chap. XVII.) was first pointed out by Turek, worked out by Schloesing, and finally applied industrially by Solvay. The first (1883) large soda factories erected in Russia for working this process are on the banks of the Kama at Bereznjak, near Ousolia, and belong to Lubimoff and Solvay. In 1890 a large factory was erected by P. K. Oushkoff on the Kama, near Elagoubi, to work the Leblanc process.

^{16a} Mond (see Chap. XI., note 3a) separates the NH_4Cl from the residual solutions by cooling (Chap. X., note 44), then ignites the sal-ammoniac and passes the vapour over MgO , and so re-obtains the NH_3 and forms MgCl_2 : the former goes back for the manufacture of soda, while the latter is employed either for making HCl or Cl_2 .

¹⁷ Commercial soda ash (calcined, anhydrous) is rarely pure; the crystallised soda is generally purer. In order to purify it further, it is shaken up with a strong solution of ammonia, and the residue recrystallised and calcined. The impurities will then remain in the mother liquors, &c.

Some numerical data may be given for sodium carbonate. The specific gravity of the anhydrous salt is 2.48, that of the decahydrated salt 1.46. Of the heptahydrated salt two varieties are known (Löwel, Marignac, Rammelsberg), which are formed by allowing a saturated solution to cool under a layer of alcohol; the one is less stable (like the corresponding sulphate) and at 0° has a solubility of 32 parts (of anhydrous salt) in 100 of water; the other is more stable, and its solubility is 20 parts (of anhydrous salt) per 100 of water. The solubility of the decahydrated salt in 100 of water is at 0° , 7.0; at 20° , 21.7; and at 30° , 37.2 parts (of anhydrous salt). At 80° the solubility is only 46.1; at 90° , 45.7; and at 100° , 45.4 parts (of anhydrous salt). That is, the solubility falls as

Sodium carbonate loses all its water on being heated, and when anhydrous fuses at a bright red heat (1098°). A small quantity of sodium carbonate placed in the loop of a platinum wire volatilises in the heat of a gas flame, and therefore in the furnaces of glass works, part of the soda is always transformed into the condition of vapour. Sodium carbonate resembles sodium sulphate in its relation to water.¹⁸ Here also the greatest solubility is at the temperature of 37° ; both salts, on crystallising at the ordinary temperature, combine with ten molecules of water, and such crystals of soda, like crystals of Glauber's salt, fuse. Sodium carbonate also forms a supersaturated solution, and, according to the conditions, gives various combinations with water of crystallisation (Chap. I., note 24).

At a red heat superheated steam liberates carbonic anhydride from sodium carbonate and forms caustic soda, $\text{Na}_2\text{CO}_3 + \text{H}_2\text{O} = 2\text{NaHO} + \text{CO}_2$. Here the carbonic anhydride is replaced by water: this depends on the feebly acid character of carbonic anhydride. By direct heating, sodium carbonate is only slightly decomposed into sodium oxide and carbonic anhydride; thus, when sodium carbonate is fused, about 1 per cent. of carbonic anhydride is disengaged.¹⁹ The carbonates of many other metals—for instance, of calcium, copper, magnesium, iron, &c.—on being heated lose all their carbonic anhydride. This shows the very considerable basic energy which sodium possesses. With the soluble salts of most metals, sodium carbonate gives precipitates either of insoluble carbonates of the metals, or else of the hydroxides (in this latter case carbonic anhydride is disengaged); for instance, with barium salts it precipitates an insoluble barium carbonate ($\text{BaCl}_2 + \text{Na}_2\text{CO}_3 = 2\text{NaCl} + \text{BaCO}_3$) and with the aluminium salts it precipitates aluminium hydroxide, carbonic anhydride being disengaged: $3\text{Na}_2\text{CO}_3 + \text{Al}_2(\text{SO}_4)_3 + 3\text{H}_2\text{O} = 3\text{Na}_2\text{SO}_4 + 2\text{Al}(\text{OH})_3 + 3\text{CO}_2$. Sodium carbonate, like all the salts of carbonic acid, evolves carbonic anhydride on treatment with all acids which are to any extent energetic. But if an acid diluted with water be gradually added to a solution of sodium

the temperature rises, like that of Na_2SO_4 . The specific gravity (note 7) of solutions of sodium carbonate (according to the data of Gerlach and Kohlrausch) at $15^{\circ}/4^{\circ}$ is expressed by the formula, $s = 9.992 + 104.5p + 0.165p^2$. Weak solutions occupy a volume not only less than the sum of the volumes of the anhydrous salt and the water, but even less than the water contained in them. For instance, 1,000 grams of a 1 per cent. solution occupy (at 15°) a volume of 990.4 c.c. (sp. gr. 1.0097), but contain 990 grams of water, occupying at 15° a volume of 990.8 c.c. Such cases are comparatively rare (but occur also with sodium hydroxide).

¹⁸ The resemblance is so great that the composition of Na_2SO_4 and Na_2CO_3 may be classed under the type $(\text{NaO})_2\text{R}$, where $\text{R} = \text{SO}_2$ or CO . Many other sodium salts also contain 10 mol. H_2O .

¹⁹ According to the observations of Pickering. According to Rose, when solutions of sodium carbonate are boiled, a certain amount of carbonic anhydride is disengaged.

carbonate, *at first* such an evolution does not take place, because the excess of the carbonic anhydride forms **acid sodium carbonate (sodium bicarbonate)**, NaHCO_3 ,²⁰ which is, however, unstable. Not only when heated alone, but even on being slightly heated in solution, and also at the ordinary temperature in damp air, it loses carbonic anhydride and forms the normal salt. And at the same time it is easy to obtain it in a pure crystalline form, if a strong solution of sodium carbonate be cooled and a stream of carbonic anhydride gas passed through it. The acid salt is less soluble in water than the normal,²¹ and therefore a strong solution of the latter gives crystals of the acid salt if carbonic anhydride be passed through it. The acid salt may be yet more conveniently formed from effloresced crystals of sodium carbonate, which, on being considerably heated, very readily absorb carbonic anhydride.²² The acid salt crystallises well, but not, however, in such large crystals as the normal salt; it has a brackish and not an alkaline taste like that of the normal salt; its reaction is feebly alkaline, nearly neutral. At 70° under the atmospheric pressure its solution begins to lose carbonic anhydride, and on boiling the evolution becomes very abundant. From

²⁰ The composition of this salt, however, may be also represented as a combination of carbonic acid, H_2CO_3 , with the normal salt, Na_2CO_3 , just as the latter also combines with water. Such a combination is all the more likely because there exists another salt, $\text{Na}_2\text{CO}_3, \text{NaHCO}_3, 2\text{H}_2\text{O}$ (sodium sesquicarbonate), obtained by cooling a boiling solution of sodium bicarbonate, or by mixing this salt with the normal salt; but the formula of this salt cannot be derived from the molecular formula of normal carbonic acid, as the formula of the bicarbonate can. At the same time the sesqui-salt has all the properties of a definite compound; it crystallises in transparent crystals, has a constant composition, and its solubility (and at 0° in 100 of water, 12.6 of anhydrous salt) differs from the solubility of the normal and acid salts; it is found in nature, and is known by the names of *trona* and *urao*. This salt is very stable in air, and may be used for purifying sodium carbonate on the large scale.

²¹ A hundred parts of water at 0° dissolve 7 parts of the acid salt, which corresponds with 4.3 parts of the anhydrous normal salt, but at 0° , 100 parts of water dissolve 7 parts of the latter. The solubility of the bi- or acid salt varies with considerable regularity; 100 parts of water dissolve, at 15° , 9 parts of the salt, and, at 30° , 11 parts.

The ammonium, and more especially the calcium, salt is much more soluble in water. The ammonia process (see p. 542) is founded upon this. Ammonium bicarbonate (acid carbonate) has at 0° a solubility of 12 parts in 100 of water, and at 30° , of 27 parts. Also its saturated solution is more stable than a solution of sodium bicarbonate. In fact, saturated solutions of these salts have a gaseous pressure like that of a mixture of carbonic anhydride and water—at 50° , for the sodium salt it is 750 millimetres, and for the ammonium salt, 563 millimetres.

²² Crystalline sodium carbonate (broken into lumps) also absorbs carbonic anhydride, but the water contained in the crystals is then disengaged: $\text{Na}_2\text{CO}_3, 10\text{H}_2\text{O} + \text{CO}_2 = 2\text{NaHCO}_3 + 9\text{H}_2\text{O}$, and dissolves part of the carbonate. When it is required to avoid the formation of this solution, a mixture of ignited and crystalline sodium carbonate is taken. Sodium bicarbonate is prepared chiefly for medicinal use, and is then often termed *carbonate of soda*, and also, for instance, in the so-called soda powders, for preparing certain artificial mineral waters, for the manufacture of digestive lozenges like those made at Essentuki, Vichy, &c.

the preceding remarks it is clear that in most reactions this salt, especially when heated, acts similarly to the normal salt, but has, naturally, some distinction from it. Thus, for example, if a solution of sodium carbonate be added to a normal magnesium salt, a turbidity (precipitate) of magnesium carbonate, MgCO_3 , is formed. No such precipitate is formed by the acid salt, because magnesium carbonate is soluble in the presence of an excess of carbonic anhydride.

Sodium carbonate is generally used for the preparation of **caustic soda** ²³—that is, the hydrate of sodium oxide, or the alkali which corresponds to sodium. For this purpose the action of lime on a solution of sodium carbonate is generally made use of. The process is as follows: a weak, generally 10 per cent., solution of sodium carbonate is taken, ²⁴ and boiled in a cast-iron, wrought-iron, or silver boiler (sodium hydroxide does not act on these metals), and lime is added, little by little, during the boiling. This latter is soluble in water, although but very slightly. The clear solution becomes turbid on the addition of the lime because a precipitate is formed; this precipitate consists of calcium carbonate, which is almost insoluble in water, whilst caustic soda is formed and remains in solution; the reaction is expressed by the equation: $\text{Na}_2\text{CO}_3 + \text{Ca}(\text{HO})_2 = \text{CaCO}_3 + 2\text{NaHO}$. After the necessary quantity of lime has been added, ²⁵ the solution is allowed to stand, and is

²³ In chemistry, sodium oxide is termed 'soda,' which word must be carefully distinguished from the word 'sodium,' meaning the metal. Commercially it is also called 'caustic soda.'

²⁴ With a small quantity of water, the reaction either does not take place, or even proceeds in the reverse way—that is, sodium and potassium hydroxides remove carbonic anhydride from calcium carbonate (Liebig, Watson, Mitscherlich, and others). The influence of the mass of water is evident. According to Gerberts, however, strong solutions of sodium carbonate are decomposed by lime, which is very interesting if confirmed by further investigation.

²⁵ As long as any undecomposed sodium carbonate remains in solution, excess of acid added to the solution disengages carbonic anhydride, and the solution after dilution gives with a barium salt a white precipitate soluble in acids, showing the presence of a carbonate in solution (if there be sulphate present, it also forms a white precipitate, but this is insoluble in acids). For the decomposition of sodium carbonate, milk of lime—that is, slaked lime suspended in water—is employed. Formerly pure sodium hydroxide was prepared (according to Berthollet's process) by dissolving the impure substance in alcohol (sodium carbonate and sulphate are not soluble), but now that metallic sodium has become cheap and is purified by distillation, *pure caustic soda* is prepared by acting on a small quantity of water with sodium (note 33a). Sodium hydroxide may also be purified by allowing strong solutions to crystallise (in the cold) (note 27).

In alkali works where the Leblanc process is used, caustic soda is prepared directly from the alkali remaining in the mother liquors after the separation of the sodium carbonate by evaporation (note 14). If excess of lime and charcoal have been used, much sodium hydroxide may be obtained. After the removal of as much as possible of the sodium carbonate, a red (from iron oxide) liquid is left, containing sodium hydroxide mixed with compounds of sulphur and of cyanogen, and also containing iron. This red alkali is evaporated and air blown through it, which oxidises the impurities (for this

then decanted off and evaporated in cast or wrought iron boilers, or, if a perfectly pure product is required, in silver pans.²⁶ The evaporation cannot be conducted in china, glass, or similar vessels, because caustic soda attacks these materials, although but slightly. The solution does not crystallise on evaporation, because the solubility of caustic soda when hot is very great, but if a concentrated solution (sp. gr. about 1.38) is cooled it deposits crystals consisting of $2\text{NaHO}, 7\text{H}_2\text{O}$, which fuse at $+6^\circ$.²⁷ If the evaporation is conducted so long as water is disengaged—which requires a considerable amount of heat—on cooling, the hydroxide, NaHO , solidifies in a semi-transparent crystalline mass,²⁸ which eagerly absorbs moisture and carbonic anhydride from the air.²⁹ Its specific gravity is 2.13, and³⁰ it is easily soluble in water, with

purpose sodium nitrate or bleaching powder, &c., is sometimes added) and leaves fused caustic soda. The fused mass is allowed to settle in order to separate the ferruginous precipitate, and is then poured into iron drums, where the sodium hydroxide solidifies. Such caustic soda contains about 10 per cent. of water in excess and some saline impurities, but when properly manufactured is almost free from carbonate and from iron. The greater part of the caustic soda, which forms so important an article of commerce, is manufactured in this manner.

²⁶ Löwig gave a method of preparing sodium hydroxide from sodium carbonate by heating it to a dull red heat with an excess of ferric oxide. Carbonic anhydride is given off, and warm water extracts the caustic soda from the remaining mass. This reaction, as experiment shows, proceeds very easily, and is an example of contact action similar to that of ferric oxide on the decomposition of potassium chlorate. In order to represent this clearly it is sufficient, for instance, to imagine that in the sodium carbonate the elements CO_2 move in a circle round the elements Na_2O , but at the points of contact with Fe_2O_3 the motion becomes elliptical with a long axis, and at some distance from Na_2O the elements of CO_2 are parted, not having the faculty of attaching themselves to Fe_2O_3 .

The action of an electric current on strong solutions of NaCl or on the fused salt gives chlorine at the anode and sodium at the cathode. If a mercury cathode is employed it dissolves the sodium, and if the amalgam is brought into contact with water or a previously formed solution of caustic soda, the whole of the sodium separates from the mercury with the evolution of hydrogen and formation of NaOH . There are many processes (Castner, Borchers, &c.) founded on this action (some employ a cathode of molten lead with fused NaCl).

²⁷ By allowing strong solutions of sodium hydroxide to crystallise in the cold, impurities—such as, for instance, sodium sulphate—may be separated from them. The fused crystallo-hydrate, $2\text{NaHO}, 7\text{H}_2\text{O}$, forms a solution having a specific gravity of 1.405 (Hermes). The crystals on dissolving in water produce cold, whilst NaHO produces heat. Besides which Pickering obtained hydrates with 1, 2, 4, 5, and 7 H_2O .

²⁸ In solid caustic soda there is generally an excess of water beyond that required by the formula NaHO . The caustic soda used in laboratories is generally cast in sticks, which are broken into pieces. It must be preserved in carefully closed vessels, because it absorbs water and carbonic anhydride from the air.

²⁹ By the way it changes in air it is easy to distinguish caustic soda from caustic potash, which in general resembles it. Both alkalies absorb water and carbonic anhydride from the air, but caustic potash forms a deliquescent mass of potassium carbonate, whilst caustic soda forms a dry powder of efflorescent salt.

³⁰ As the molecular weight of NaHO is 40, the volume of its molecule is $40 \cdot 2.13$, that is, 18.5, which very nearly approaches the volume of a molecule of water. The same rule

disengagement of a considerable quantity of heat.³¹ A saturated solution at the ordinary temperature has a specific gravity of about 1.5, contains about 45 per cent. of sodium hydroxide, and boils at 130°; at 55° water dissolves an equal weight of it.³² Caustic soda is not only soluble in water, but also in alcohol, and even ether. Dilute solutions of sodium hydroxide produce a soapy feeling on the skin because the active base of soap consists of caustic soda.³³ Strong solutions have a corroding action on animal tissues. As the NaHO prepared from soda always contains some impurities (soda, sulphuric acid, &c.), which it is difficult to separate entirely, and as it absorbs CO₂ from the

applies to the compounds of sodium in general—for instance, its salts have a molecular volume approaching the volume of the acids from which they are derived.

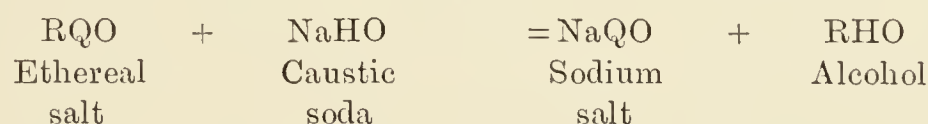
³¹ The molecular quantity of sodium hydroxide (40 grams), on being dissolved in a large mass (200 gram molecules) of water, develops, according to Berthelot, 9,780, and, according to Thomsen, 9,940, heat units. Solutions of NaHO + n H₂O, on being mixed with water, evolve heat if they contain less than 6H₂O, but absorb it if they contain more.

³² The specific gravity of solutions of sodium hydroxide at 15°/4° is given in the short table below:

NaHO, per cent.	.	5	10	15	20	30	40
Sp. gr.	.	1.057	1.113	1.169	1.224	1.331	1.436

1,000 grams of a 5 per cent. solution occupy a volume 946 c.c.; that is, less than the water serving to make the solution (see note 18).

³³ Sodium hydroxide and some other alkalies are capable of hydrolysing—saponifying, as it is termed—the compounds of acids with alcohols. If RHO [or R(HO) _{n}] represent the composition of an alcohol—that is, of the hydroxide of a hydrocarbon radicle—and QHO an acid, then the compound of the acid with the alcohol or the ethereal salt of the given acid will have the composition RQO. Ethereal salts, therefore, present a likeness to metallic salts, just as alcohols resemble basic hydroxides. Sodium hydroxide acts on ethereal salts in the same way as it acts on the majority of metallic salts—namely, it liberates alcohol, and forms the sodium salt of the acid contained in the ethereal salt. The reaction takes place in the following way:



Such a decomposition is termed **saponification**. Similar reactions were known very long ago, for the ethereal salts corresponding with glycerin, C₃H₅(OH)₃, are found (in animals and plants) as fats and oils. Caustic soda, acting on fat and oil, forms glycerin and the sodium salts of those acids which were in union with the glycerin in the fat, as Chevreul showed at the beginning of the last century. The sodium salts of the fatty acids are commonly known as **soaps**. That is to say, soap is made from fat and caustic soda, glycerin being separated and a sodium salt or soap formed. As glycerin is usually found in union with certain acids, so also are the sodium salts of the same acids found in soap. The greater part of the acids found in conjunction with glycerin in fats consists of the solid palmitic and stearic acids, C₁₆H₃₂O₂ and C₁₈H₃₈O₂, and the liquid oleic acid, C₁₈H₃₄O₂. Water acting on soap partly decomposes it (because the acids of the soap are feeble), and the alkali set free acts during the application of the soap. Hence it may be replaced by a very feeble alkali. Strong solutions of alkali corrode the skin and tissues. The reaction of the alkali with the acids contained in soap is reversible, and the alkali is only set free by the excess of water, according to the teaching of Berthollet.

atmosphere, pure caustic soda is now often prepared by the action of metallic sodium upon water, $2\text{Na} + 2\text{H}_2\text{O} = 2\text{NaHO} + \text{H}_2$,^{33a} and this reagent may now be bought ready made.

The chemical **reactions of sodium hydroxide** serve as a type for those of a whole class of alkalies—that is, of soluble basic hydroxides, MOH. The solution of sodium hydroxide is a very caustic liquid—that is to say, it acts in a destructive way on most substances, for instance, organic tissues. Hence caustic soda, like all soluble alkalies, is a poisonous substance; acids, for example, hydrochloric, serve as antidotes. The action of caustic soda on bones, fat, starch, and similar vegetable and animal substances explains its action on organisms. Thus bones, when plunged into a weak solution of caustic soda, fall to powder³⁴ and evolve a smell of ammonia, owing to the caustic soda changing the gelatinous organic substance of the bones (which, like albumin, contains carbon, hydrogen, nitrogen, oxygen, and sulphur), dissolving it and in part destroying it, whence ammonia is disengaged. Fats, tallow, and oils become saponified by a solution of caustic soda—that is to say, they form with it **soaps** soluble in water, or sodium salts of the organic acids contained in the fats.³⁵ The most characteristic reactions of sodium hydroxide are determined by the fact that it **saturates all acids, forming with them salts**, which are almost all soluble in water, and in this respect caustic soda is as characteristic among the bases as nitric acid among the acids. It is impossible to detect sodium by means of the formation of precipitates of insoluble sodium salts, as may be done with other metals, many of whose salts are but slightly soluble. The powerful alkaline properties of caustic soda determine its capacity for combining with even the feeblest acids, its property of disengaging ammonia from ammonium salts, its faculty of forming precipitates from solutions of salts of bases insoluble in water, &c. If a solution of the salt of almost any metal be mixed with caustic soda, a soluble sodium salt will be formed, and an insoluble hydroxide of the metal separated—for instance, copper nitrate yields copper hydroxide, $\text{Cu}(\text{NO}_3)_2 + 2\text{NaHO} = \text{Cu}(\text{HO})_2 + 2\text{NaNO}_3$. Even many

^{33a} It is prepared in a silver basin, cooled from the outside by water. A little water is first poured into the basin and sodium carefully added a little at a time, the basin being continually rocked to prevent any of the sodium attaching itself to the sides (which might be followed by an explosion). When a solution of caustic soda is already formed, the reaction proceeds more quietly, especially if the dish be cooled outside. It is still better to take alcohol and add the water and sodium gradually to it.

³⁴ On this is founded the process of Henkoff and Engelhardt for treating bones. The bones are mixed with ashes, lime, and water; it is true that in this case more potassium hydroxide than sodium hydroxide is formed, but the action is almost identical.

³⁵ As explained in note 33.

basic oxides precipitated by caustic soda **are capable** of combining with it and forming soluble compounds, and therefore caustic soda in the presence of salts of such metals first forms a precipitate of hydroxide, and then, employed in excess, dissolves this precipitate. This phenomenon occurs, for example, when caustic soda is added to the salts of aluminium. This shows the property of such an alkali as caustic soda of combining, not only with acids, but also with feeble basic oxides. For this reason caustic soda **acts on most elements** which are capable of forming acids or feeble bases; thus the metal aluminium gives hydrogen with caustic soda in consequence of the formation of alumina, which combines with the caustic soda—that is, in this case, the caustic alkali acts on the metal just as sulphuric acid does on Fe or Zn. If caustic soda acts in this manner on a metalloid capable of combining with the hydrogen evolved (aluminium does not give a compound with hydrogen), then such a hydrogen compound is formed. Thus, for instance, phosphorus acts in this way on caustic soda, yielding hydrogen phosphide. When the hydrogen compound disengaged is capable of combining with the alkali, then, naturally, a salt of the corresponding acid is formed. For example, chlorine and sulphur act in this way on caustic soda. Chlorine, with the hydrogen of the caustic soda, forms hydrochloric acid, and the latter forms common salt with the sodium hydroxide, while the other atom in the molecule of chlorine, Cl_2 , takes the place of the hydrogen, and forms the hypochlorite, NaClO . In the same way, by the action of sodium hydroxide on sulphur, hydrogen sulphide is formed, which acts on the soda and forms sodium **sulphide** (in addition to which sodium thiosulphate is also formed; see Chap. XX.). The action is often accelerated by the presence of the oxygen of the air, as by this means the formation of acids and oxides rich in oxygen is facilitated. Thus many metals and their lower oxides, in the presence of NaHO , absorb oxygen and form acids. Even manganese dioxide, when mixed with caustic soda, is capable of absorbing the oxygen of the air and forming sodium manganate, Na_2MnO_4 . Organic acids when heated with caustic soda give up to it the elements of carbonic anhydride, forming sodium carbonate, and separate that hydrocarbon group which exists, in combination with carbonic anhydride, in the organic acid.

Thus sodium hydroxide, like the soluble alkalies in general, ranks amongst the most chemically active substances, and but few substances are capable of resisting it. Even silicious rocks, as we shall see further on, are transformed by it and form vitreous slags when fused with it. Sodium hydroxide (like ammonium and potassium hydroxides), as a typical example of the basic hydrates, in distinction from many other

basic oxides, readily **forms acid salts** with acids (for instance, NaHSO_4 , NaHCO_3), and forms no basic salts at all; whilst many less energetic bases, such as the oxides of copper and lead, form basic salts easily, but acid salts only with difficulty. This capability of forming acid salts, particularly with polybasic acids, may be explained by the energetic basic properties of sodium hydroxide, contrasted with the small development of these properties in those bases which easily form basic salts. An energetic base is capable of retaining a considerable quantity of acid, which a slightly energetic base would not have the power of doing. Also, as will be shown in subsequent chapters, sodium belongs to the univalent metals, being exchangeable for hydrogen, atom for atom—that is, amongst metals sodium may, like chlorine amongst the non-metals, serve as the representative of the univalent properties. Most of the elements which are not capable of forming acid salts are divalent. Whence it may be gathered that in a dibasic acid—for instance, carbonic, H_2CO_3 , or sulphuric, H_2SO_4 —the hydrogen may be exchanged, atom for atom, for sodium, and yield an acid salt by means of the first substitution, and a normal salt by means of the second—for instance, NaHSO_4 , and Na_2SO_4 —whilst such bivalent metals as calcium and barium do not form acid salts, because one of their atoms at once takes the place of both hydrogen atoms, forming, for example, CaCO_3 and CaSO_4 .^{35a}

We have seen the transformation of common salt into sodium sulphate, of this latter into sodium carbonate, and of sodium carbonate into caustic soda. Lavoisier regarded sodium hydroxide as an element, because he was unacquainted with its decomposition with the formation of metallic sodium, which separates the hydrogen from water, re-forming caustic soda.

The preparation of **metallic sodium** was one of the greatest dis-

^{35a} It might be expected, from what has been mentioned above, that divalent metals would easily form acid salts with acids containing more than two atoms of hydrogen—for instance, with tribasic acids, such as phosphoric acid, H_3PO_4 —and such salts actually exist; but all such relations are complicated by the fact that the character of the base very often changes and becomes weakened with the increase of valency and the change of atomic weight; the feebler bases (like silver oxide), although corresponding with univalent metals, do not form acid salts, while the feeblest bases (CuO , PbO , &c.) readily form basic salts, and notwithstanding their valency do not form acid salts which are in any degree stable—that is, which are undecomposable by water. Basic and acid salts ought to be regarded rather as compounds similar to crystallo-hydrates, because such acids as sulphuric form with sodium, not only an acid and a normal salt, as might be expected from the valency of sodium, but also salts containing a greater quantity of acid. In sodium sesquicarbonate we saw an example of such compounds. Taking all this into consideration, we must say that the property of more or less easily forming acid salts depends more upon the energy of the base than upon its valency, and the best statement is that *the capacity of bases for forming acid and basic salts is characteristic of them*, just as the faculty of forming compounds with hydrogen is characteristic of elements.

coveries in chemistry, not only because through it the conception of elements became broader and more correct, but especially because in sodium, chemical properties were observed which were but feebly shown by the other metals more familiarly known. This discovery was made in 1807 by the English chemist **Davy** by means of the galvanic current. By connecting with the positive pole (of copper or carbon) a piece of caustic soda (moistened in order to obtain electrical conductivity), and boring a hole in it filled with mercury connected with the negative pole of a strong Volta's pile, Davy observed that on passing the current a peculiar metal dissolved in the mercury, less volatile than mercury, and capable of decomposing water, again forming caustic soda. In this way (by analysis and synthesis) Davy demonstrated the compound nature of alkalis. On being decomposed by the galvanic current, caustic soda disengages hydrogen and sodium at the negative pole and oxygen at the positive pole. Davy showed that the metal formed volatilises at a red heat, and this is its most important physical property in relation to its extraction, all later methods being founded on it. Besides this Davy observed that sodium easily oxidises, its vapour taking fire in air, and the latter circumstance was for a long time an obstacle to the easy preparation of this metal. The properties of sodium were subsequently more thoroughly investigated by Gay-Lussac and Thénard, who observed that metallic iron at a high temperature was capable of reducing caustic soda to sodium.³⁶ Brunner latterly discovered that not only iron, but also charcoal, has this property, although hydrogen has not.³⁷ But still the methods of extracting sodium were very troublesome, and consequently it was a great rarity. The

³⁶ Deville supposes that such a decomposition of sodium hydroxide by metallic iron depends solely on the dissociation of the alkali at a white heat into sodium, hydrogen, and oxygen. Here the part played by the iron is only that it retains the oxygen formed, otherwise the decomposed elements would again reunite upon cooling, as in other cases of dissociation. If it be supposed that the temperature at the commencement of the dissociation of the iron oxides is higher than that of sodium oxide, the decomposition may be explained by Deville's hypothesis. Deville demonstrates his views by the following experiment:—an iron bottle, filled with iron borings, was heated in such a way that the upper part became red hot, the lower part remaining cooler; sodium hydroxide was introduced into the upper part. The decomposition was then effected—that is, sodium vapours were produced (this experiment was really performed with potassium hydroxide). On opening the bottle it was found that the iron in the upper part was not oxidised, but only that in the lower part. This may be explained by the decomposition of the alkali into sodium, hydrogen, and oxygen taking place in the upper part, whilst the iron in the lower part absorbed the oxygen set free. If the whole bottle is subjected to the same moderate heat as the lower extremity, no metallic vapours are formed. In that case, according to the hypothesis, the temperature is insufficient for the dissociation of the sodium hydroxide.

³⁷ It has been previously remarked (Chap. II., note 9) that Beketoff showed the displacement of sodium by hydrogen, not from sodium hydroxide, but from the oxide Na_2O , when, however, only one half is displaced, with the formation of NaHO .

principal obstacle to its production was that an endeavour was made to condense the easily oxidising vapours of sodium in vacuo in complicated apparatus. For this reason, when Donny and Maresca, having thoroughly studied the matter, constructed a specially simple condenser, the production of sodium was much facilitated. The production of sodium was yet further simplified by Sainte-Claire Deville, who employed a mixture of anhydrous sodium carbonate (7 parts), charcoal (2 parts), and lime or chalk (7 parts). This latter ingredient is only added in order that the sodium carbonate, on fusing, shall not separate from the charcoal.³⁸ The chalk on being heated loses carbonic anhydride, leaving infusible lime, which is permeated by the sodium

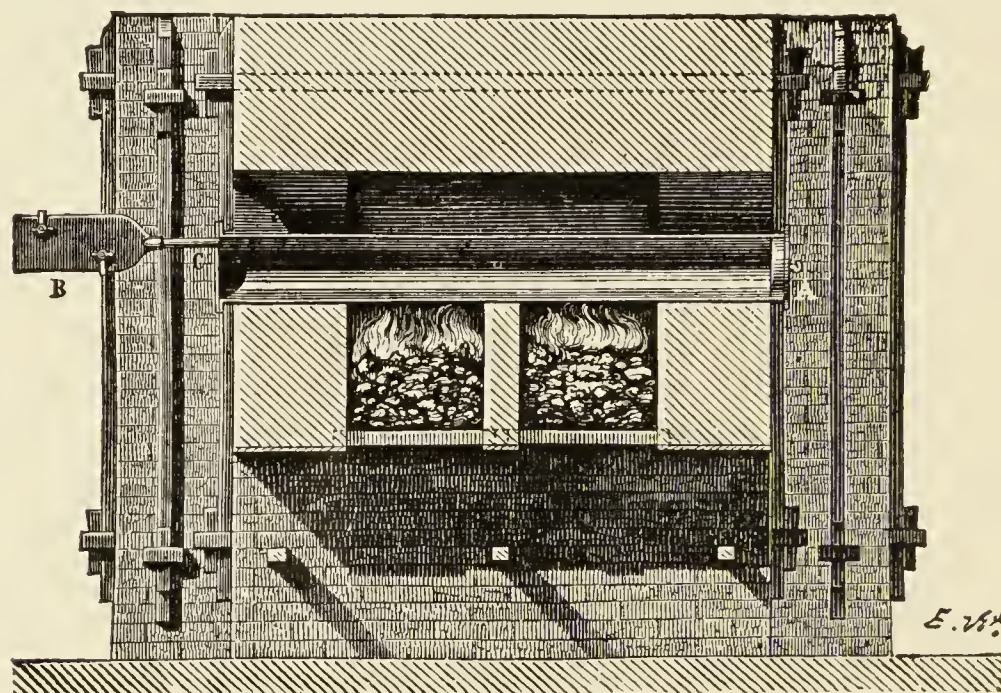
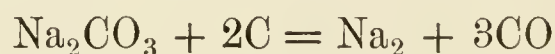


FIG. 80.—Manufacture of sodium by Deville's process. A C, iron tube containing a mixture of soda, charcoal, and chalk. B, condenser.

carbonate and forms a thick mass, in which the charcoal is intimately mixed with the sodium carbonate. When the charcoal is heated with the sodium carbonate, at a white heat, carbonic oxide and vapours of sodium are disengaged, according to the equation :



In sodium works, an iron tube, about a metre long and a decimetre in diameter, made of boiler plate, is luted into a furnace having a strong

³⁸ Since the close of the eighties in England, where the preparation of sodium is at present carried out on a large commercial scale (from 1860 to 1870 it was only manufactured in a few works in France), it has been the practice to add iron to Deville's mixture; with the charcoal this gives carburetted iron, which still further facilitates the decomposition. Thus Castner heated a mixture of 44 parts of NaHO and 7 parts of carbide of iron in large iron retorts at 1,000° and obtained about 6½ parts of metallic sodium. The reaction proceeds more easily than with carbon or iron alone. Subsequently, in 1891, aluminium was prepared by electrolysis (see Chap. XVII.), and metallic sodium found new uses : for the manufacture of peroxide of sodium (see later on), for the manufacture of potassium and sodium cyanide from yellow prussiate (Chap. XIII., note 12), and for the preparation of pure NaHO, &c.

draught, capable of giving a high temperature, and is charged with the mixture required for the preparation of sodium. One end of the tube is closed with a cast-iron stopper A with clay luting, and the other with the cast-iron stopper C provided with an aperture. On heating, the moisture contained in the various substances is first given off, then carbonic anhydride and the products of the dry distillation of the charcoal, after which carbonic oxide and vapours of sodium appear. It is easy to observe the appearance of the latter, because on issuing from the aperture in the stopper C they take fire spontaneously and burn with a very bright yellow flame. The pipe of the condenser is then introduced into the aperture C. This condenser consists of two square cast-iron trays, A and A', fig. 81, with wide edges firmly screwed together. Between these two trays there is a space in which the condensation of the vapours of sodium is effected, the thin metallic walls of the condenser being cooled by the air but remaining hot enough to preserve the sodium in a liquid state, so that it does not choke the apparatus, but continually flows from it. The vapours of sodium, condensing in the cooler, flow in the shape of liquid metal into a vessel containing some difficultly volatile hydrocarbon (heavy naphtha oils). This is used in order to prevent the sodium oxidising as it issues from the condenser at the somewhat high temperature at which it escapes. In order to obtain sodium of a pure quality it is necessary to distil it once more; this may even be done in porcelain retorts, but the distillation must be conducted in a stream of some gas on which sodium does not act; for instance, in a stream of nitrogen; carbonic anhydride is not applicable, because sodium partially decomposes it, absorbing oxygen from it.^{38a}

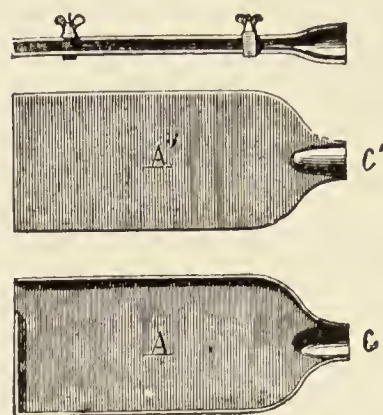


FIG. 81.—Donny and Maresca's sodium condenser, consisting of two cast-iron plates screwed together.

Pure sodium is a lustrous metal, at the ordinary temperature as white as silver and as soft as wax, but it becomes brittle in the cold. In ordinary moist air it quickly tarnishes and becomes covered with a film of NaHO and Na_2CO_3 , formed at the expense of the water and CO_2 in the air. In perfectly dry air sodium retains its lustre for an indefinite time. Its density at the ordinary temperature is equal to 0.975, so that it is lighter than water; it fuses very easily at a temperature of 97° , and distils at a bright red heat (742° , according to Perman, 1889).

^{38a} The manufacture of metallic sodium by electrolysis, which has been tried in different ways, has not, as far as I know, proved as economical and convenient as the direct reduction of soda by a mixture of carbon and iron. Sodium is sometimes sold in lumps coated with paraffin.

Scott (1887) determined the density of sodium vapour and found it to be nearly 12 (if $H = 1$). This shows that its molecule contains one atom (like mercury and cadmium), Na.³⁹ It fuses with most metals, forming indefinite compounds called alloys. Thus, if sodium, having a clean surface) be thrown into mercury, especially when heated, there is a flash, and such a considerable amount of heat is evolved that part of the mercury is transformed into vapour.^{39a} Compounds or solutions of sodium in mercury, or **amalgams** of sodium, even when containing only 2 parts of sodium to 100 parts of mercury, are solid. Only those amalgams which are the very poorest in sodium are liquid. Such alloys of sodium with mercury⁴⁰ are often used instead of sodium in chemical

³⁹ This is also shown by the fall in the temperature of solidification of tin produced by the addition of sodium (and also Al and Zn); Heycock and Neville (1889).

^{39a} By dissolving sodium amalgams in water and acids, and deducting the heat of reaction of the sodium, Berthelot found that *for each atom of the sodium* in amalgams containing a larger amount of mercury than corresponds with NaHg₅, the amount of heat evolved increases, after which the heat of formation falls, and the heat evolved decreases. In the formation of NaHg₅ about 18,500 calories are evolved; when NaHg₃ is formed, about 14,000; and for NaHg about 10,000 calories. Kraft regarded the definite crystalline amalgam as having the composition of NaHg₆, but in accordance with Grimaldi's results, it is thought to be NaHg₅. A similar amalgam is very easily obtained if a 3 per cent. amalgam be left several days in a solution of sodium hydroxide until a crystalline mass is formed, from which the mercury may be removed by strongly pressing in chamois leather.

⁴⁰ Alloys are so similar to solutions that what is known for solutions may be applied to alloys and conversely. But in alloys, as substances passing from the liquid to the solid state, it is easier to discover the formation of definite chemical compounds. Their presence in alloys is not only proved by their being seen in the form of separate crystals, but also by a systematic investigation of any (physical and chemical) property of alloys presenting the most diverse composition; for instance, by investigating the melting-points, the heat evolved, the variation in volume (sp. gr.), electro-motive force, &c. Thus Prof. Kurnakoff in his researches on the alloys of Na with Hg, Cd, Pb, and Bi (1900) determined their fusing-points, and in this way found those definite compounds which are mentioned above. In general the alloys of sodium, owing to the comparative energy and peculiar properties of the metal, have been closely studied by Bailey (1892), Joannis (1892), Maly (1899), and others, and all recognised the formation of one or even several definite compounds in them, and the same is observed with almost any pair of metals. It is my personal opinion that this universal phenomenon (the formation of definite compounds between metals) in alloys speaks much in favour of the fact that definite compounds should also be formed in the intermixture of liquids (for instance, of alcohol or sulphuric acid with water) and in the solution of salts in water. As the formation of definite compounds in metallic alloys was known long ago, I endeavoured when investigating solutions (Chap. I.) to trace the formation of definite compounds in them also. In speaking of alloys and solutions in different parts of this work I only wish to point out the great interest these classes of compounds present, but details of this complex subject must be looked for in special works and text-books on physical chemistry, especially because they deal fully with the doctrine of phases (see note 4), in which connection solutions and alloys are most frequently studied at the present day. For I consider that the study of solutions and particularly of alloys, which is still in its infancy (as it is chiefly occupied in describing observations and in giving a picture of individual cases, and not in making predictions and generalisations), will in

investigations, because in combination with mercury sodium is not easily acted on by air, and is heavier than water, whilst at the same time it retains its principal properties, such, for instance, as the power to decompose water, forming NaHO.

It is easy to form alloys of mercury and sodium having a crystalline structure and a definite atomic composition. One of the most remarkable is the alloy having the composition NaHg₂, which fuses at +346° (N. S. Kurnakoff, 1900), although it contains Na and Hg which fuse at far lower temperatures, namely, 97° and -39° respectively. The alloy Na₂Hg (or Na₅Hg₂) crystallises in hexagonal plates and fuses at about 105°; that having the composition NaHg fuses at about 209°, while NaHg₅ fuses at 149°. This shows that all these alloys are more difficultly fusible than their component elements, which clearly proves that new chemical compounds are formed here as in many other alloys: this is confirmed by the fact that small additions of Hg to Na (for instance, in the formation of the alloy with 40 per cent. of Hg) lower the melting-point of sodium,^{40a} just as the addition of a salt to water lowers its freezing-point.

Metallic sodium has the power of dissolving—at low temperatures and without the evolution of hydrogen—in liquefied ammonia, forming a blue solution which at 0° deposits a copper-red compound, NH₃Na (as it were, substituted ammonium). This compound has been the subject of many researches, and was studied by Weil, Joannis, and Moissan (see Chap. VI., note 14).

The peculiar chemical energy proper to sodium as an element and a metal is not only expressed in its capacity of easily displacing hydrogen from water and hydroxyl to form an energetic alkali, and in its tendency to combine with many metals with the evolution of heat, but also in many other reactions leading to the formation of saline and energetic compounds. Among these we shall now turn our attention to the compounds of sodium with hydrogen⁴¹ and oxygen.

time explain much in respect to chemical forces and phenomena. It will then have to take its place in every elementary work on chemistry, but for the present we must limit ourselves to cursory notes on this yet little cultivated field of chemistry which promises such an abundant harvest in the future.

^{40a} The alloy of 100 grams of Na with 167 grams of Hg fuses 8·8° lower than sodium, and that with 147 grams of Hg 73·0° lower (i.e., at 23·4°), so that the fall (depression) is 0·497° per gram of Hg.

⁴¹ Potassium forms a similar compound with hydrogen, but lithium apparently, as far as is known, does not react; on the other hand, neither Na nor K combines directly with nitrogen, but lithium absorbs nitrogen. Hydrazoic acid, HN₃, has a corresponding salt, NaN₃, which easily decomposes, while the two above-mentioned remarkable substances, the amide of sodium NaH₂N (note 44a) and the blue liquid containing Na(NH₃)_n (Chap. VI., note 14), which is only stable at low temperatures in the presence of an excess of NH₃, both correspond to ammonia. Moissan (1897) passed acetylene

In 1874 Troost and Hautefeuille observed that sodium, which does not react at all with hydrogen at the ordinary temperature, absorbs this gas (238 vols. per 1 vol. of Na) at temperatures of 300° to 420° ; the volume of the metal increases and the hydrogen is not evolved on cooling, but dissociation takes place above 320° .⁴² It is evident that **hydride of sodium** is formed;⁴³ but it was only obtained pure by Moissan in 1902, when he placed metallic sodium in an iron tube heated from below to 360° and cooled from above, and passed dry hydrogen through it. The hydride of sodium (NaH) formed then settles on the cooler portion of the tube as a colourless crystalline sublimate. The NaH thus obtained easily oxidises in the air and reacts vigorously with chlorine, oxygen (burns in it), and many other gases and liquids. With NH_3 gas it forms an amide, NH_2Na , liberating hydrogen. With carbonic anhydride it directly gives sodium formate according to the equation: $\text{NaH} + \text{CO}_2 = \text{CHNaO}_2$. With methyl chloride it forms NaCl and CH_4 , and with C_2H_5 it gives C_2H_6 . These peculiar properties of sodium hydride appear the more remarkable when they are compared with the properties of other hydrides, and it may not be superfluous to note that HCl and NaH, corresponding to the molecule of free hydrogen H_2 , also correspond to NaCl, as should follow from the law of substitution and from the fact that H, Cl, and Na are all monatomic (univalent or uni-equivalent).

The most important chemical property of sodium is its power of easily decomposing water and **evolving hydrogen** from the majority of the hydrogen compounds, and especially from all acids and hydrates in which the presence of hydroxyl must be recognised. This depends on its power of combining with the elements which are in combination with

through this blue liquid and obtained a colourless liquid containing an acetylene derivative of sodium, C_2NaH , with the formation of NH_3 and ethylene (see Chap. XIV., note 62), which when heated gave C_2H_2 and *carbide of sodium*, C_2Na_2 , corresponding to acetylene. The compounds of Na with H, C, and N which have recently become known—thanks to the researches of Moissan—present a series of peculiar and remarkable reactions, and will probably serve as a means for many syntheses at some future time.

⁴² The dissociation pressures p of the hydrogen in millimetres of mercury are:

	$t = 330^{\circ}$	350°	400°	430°
for the compound of Na; $p = 28$		57	447	910
„ „ „ „ K 45		72	548	1100

⁴³ Troost and Hautefeuille gave the composition Na_3H to the compound and assumed that the phenomenon resembled the formation of alloys, i.e., that the hydrogen was contained as a metal, and that the sp. gr. of the alloy was 0.959 (whence the density of hydrogen would be 0.6, which is hardly probable). Moissan showed that NaH does not react with liquid ammonia, and as the sodium in it dissolves, this may be taken advantage of for removing the sodium and separating NaH from metallic sodium which has absorbed hydrogen and contains NaH in solution.

the hydrogen. We already know that sodium disengages hydrogen, not only from water, hydrochloric acid,⁴⁴ and all other acids, but also from ammonia,^{44a} with the formation of sodamide, NH_2Na , although it does not displace hydrogen from the hydrocarbons.⁴⁵ Sodium burns both in chlorine and in oxygen, evolving much heat. These properties are closely connected with its power of **taking up oxygen, chlorine,** and similar elements from most of their compounds. Just as it removes the oxygen from the oxides of nitrogen and from carbonic anhydride, so also does it decompose the majority of oxides at definite temperatures. Here the action is essentially the same as in the decomposition of water. Thus, for instance, when acting on magnesium chloride the

⁴⁴ H. A. Schmidt remarked that perfectly dry hydrogen chloride is decomposed with great difficulty by sodium, although the decomposition proceeds easily with potassium and with sodium in moist hydrogen chloride. Wanklyn also remarked that sodium burns with great difficulty in dry chlorine.

^{44a} **Sodamide**, NHNa (Chap. IV., note 14), discovered by Gay-Lussac and Thénard, has been fully investigated by A. W. Titherley (1894).

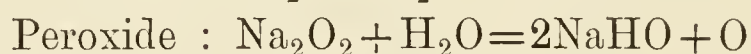
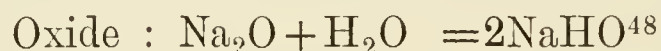
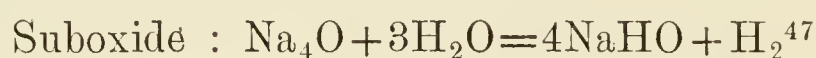
By heating sodium in dry ammonia, Gay-Lussac and Thénard obtained an olive-green readily fusible mass, **sodamide**, NH_2Na , hydrogen being separated. This substance with water forms sodium hydroxide and ammonia; with carbonic oxide, CO , it forms sodium cyanide, NaCN , and water, H_2O ; and with dry hydrogen chloride it yields sodium and ammonium chlorides. When heated, sodamide, NH_2Na , only partially decomposes, with evolution of hydrogen, the principal part of it giving ammonia and sodium nitride, Na_3N , according to the equation: $3\text{NH}_2\text{Na} = 2\text{NH}_3 + \text{NNa}_3$. The latter is an almost black powdery mass, decomposed by water into ammonia and sodium hydroxide.

According to Titherley's researches, iron or silver vessels should be used in preparing this body, because glass and porcelain are corroded at 300° – 400° , at which temperature ammonia gas acts upon sodium and forms the amide, with the evolution of hydrogen. The reaction proceeds slowly, but is complete if there be an excess of NH_3 . Pure NH_2Na is colourless (its coloration is due to various impurities), semi-transparent, shows traces of crystallisation, has a conchoidal fracture, and melts at 145° . Judging from the increase in weight of the sodium and the quantity of hydrogen which is disengaged, the composition of the amide is exactly NH_2Na . It partially volatilises (sublimes) in vacuo at 200° , and breaks up into $2\text{Na} + \text{N}_2 + 2\text{H}_2$ at 500° . NaHO is also formed to some extent by the resultant H_2O . Potassium and lithium form similar amides. With water, alcohol, and acids, NH_2Na gives NH_3 and NaHO , which react further. Anhydrous CaO absorbs NH_2Na when heated without decomposing it. When sodamide is heated with SiO_2 , NH_3 is disengaged, and silicon nitride formed. It acts still more readily upon boric anhydride when heated with it: $2\text{NH}_2\text{Na} + \text{B}_2\text{O}_3 = 2\text{BN} + 2\text{NaHO} + \text{H}_2\text{O}$. When slightly heated, $\text{NH}_2\text{Na} + \text{NOCl} = \text{NaCl} + \text{N}_2 + \text{H}_2\text{O}$ (NHNa_2 and NNa_3 are apparently not formed at a higher temperature). The organic halogen compounds react with the aid of heat, but with so much energy that the reaction frequently leads to the ultimate destruction of the organic groups and production of carbon.

⁴⁵ As sodium does not displace hydrogen from the hydrocarbons, it **may be preserved** in liquid hydrocarbons. **Naphtha** is generally used for this purpose, as it consists of a mixture of various liquid hydrocarbons. However, in naphtha sodium usually becomes coated with a crust composed of matter produced by the action of the sodium on certain of the substances contained in the liquid mixture. In order that sodium may retain its lustre in naphtha, secondary octyl alcohol is added. (This alcohol is obtained by distilling castor oil with caustic potash.) Sodium keeps well in a mixture of pure benzene and paraffin.

sodium displaces the magnesium. Sulphur, phosphorus, arsenic, and a whole series of other elements also combine with sodium.⁴⁶

With **oxygen** sodium unites in three degrees of combination, forming a suboxide Na_4O ,^{46a} an oxide, Na_2O , and a peroxide, NaO . They are thus termed because Na_2O is a stable basic oxide (with water it forms a basic hydroxide), whilst Na_4O and NaO do not form corresponding saline hydrates and salts. The suboxide is a grey inflammable substance which decomposes water, disengaging hydrogen; it is formed by the slow oxidation of sodium at the ordinary temperature. The peroxide is a yellow substance, fusing at a bright red heat; it is produced by burning sodium in an excess of oxygen, and it yields oxygen when treated with warm water:



The oxidation of sodium, under the action of heat in air or oxygen, leads only to the formation of **sodium peroxide** NaO (or Na_2O_2)

⁴⁶ Although sodium does not directly displace the hydrogen in hydrocarbons, still by indirect means compounds may be obtained which contain sodium and hydrocarbon groups. Some of these compounds have been produced, although not in a pure state. Thus, for instance, zinc ethyl, $\text{Zn}(\text{C}_2\text{H}_5)_2$, when treated with sodium, loses zinc and forms **sodium ethyl**, $\text{C}_2\text{H}_5\text{Na}$, but this decomposition is not complete, and the compound formed cannot be separated by distillation from the remaining zinc ethyl. In this compound the energy of the sodium is clearly manifest, for it reacts with substances containing haloids, oxygen, &c., and directly absorbs carbonic anhydride, forming a salt of a carboxylic acid (propionic).

^{46a} It is even doubtful whether the suboxide exists (see note 47).

⁴⁷ A compound, Na_2Cl , which corresponds with the suboxide, is apparently formed when a galvanic current is passed through fused common salt; the sodium liberated dissolves in the common salt, and does not separate out either on cooling or on treatment with mercury. It is therefore supposed to be Na_2Cl ; especially as the mass obtained gives hydrogen when treated with water: $\text{Na}_2\text{Cl} + \text{H}_2\text{O} = \text{H} + \text{NaHO} + \text{NaCl}$, that is, it acts like suboxide of sodium. If Na_2Cl really exists as a salt, then the corresponding base Na_4O , according to the rule with other bases of the composition M_4O , ought to be called a *quaternary oxide*.

⁴⁸ According to observations easily made, sodium when fused in air oxidises but does not burn, the combustion only commencing with the formation of vapour—that is, when considerably heated. Davy and Karsten obtained the oxide of sodium, Na_2O , by heating the metal with the hydroxide, when $\text{NaHO} + \text{Na} = \text{Na}_2\text{O} + \text{H}$, but N. N. Beketoff failed to obtain the pure oxide by this means. He prepared it by directly igniting the metal in dry air, afterwards heating with the metal in order to destroy the peroxide. The oxide produced, Na_2O , when heated in an atmosphere of hydrogen, gave a mixture of sodium and its hydroxide: $\text{Na}_2\text{O} + \text{H} = \text{NaHO} + \text{Na}$ (see Chap. II., note 9). Sodium oxide ought to be formed during the decomposition of sodium carbonate by oxide of iron (see note 26), and during the decomposition of sodium nitrite. According to Karsten, its specific gravity is 2.8, according to Beketoff, 2.3. The difficulty in obtaining it is owing to an excess of sodium forming the suboxide, and an excess of oxygen the peroxide.

as a yellowish mass. If it be carefully (without raising the temperature) dissolved in water at the ordinary temperature and rapidly cooled, it forms scaly crystals having the composition, $\text{NaO}, 4\text{H}_2\text{O}$, which may, like the peroxide itself, be kept unaltered in a closed vessel. But the CO_2 and water of the air act upon NaO and convert it into NaHO and Na_2CO_3 . Peroxide of sodium forms peroxide of hydrogen with acids, and then acts as an oxidising agent like the latter, but it does not part with its oxygen when heated, although it easily parts with it to substances capable of being oxidised.⁴⁹

Both Na_4O and NaO form sodium hydroxide with water, but only the oxide Na_2O is directly transformed into a hydrate. The other oxides liberate either hydrogen or oxygen: they also present a similar distinction with reference to many other agents. Thus carbonic anhydride combines directly with the oxide Na_2O , which when heated in the gas burns, forming sodium carbonate, whilst the peroxide yields oxygen in addition. When treated with acids, sodium and all its oxides form only the salts corresponding with sodium oxide—that is, of the formula or type NaX . Thus the oxide of sodium, Na_2O is **the salt-forming oxide** of this metal, just as water is in the case of hydrogen.

⁴⁹ Peroxide of sodium is now prepared on a large scale (by the action of air upon Na at 300°) for bleaching wool, silk, &c. (when it acts in virtue of the H_2O_2 formed). In preparing it on a large scale, aluminium vessels are used (Castner), and care is taken to prevent the metal taking fire (oxidation proceeds from the surface) and to keep the temperature in the furnaces below 450° (to preserve the aluminium vessels, which are not acted upon either by the sodium taken or by the peroxide). To ensure this the fresh air is only brought into contact with the vessels containing sodium in which the oxidation is completed, and the unoxidised metal is only oxidised by air from which the greater portion of the oxygen has already been exhausted. If NaNO_3 is melted, it gives Na_2O_2 with metallic Na . In a fused state the peroxide is reddish-yellow, but it becomes almost colourless when cold. When heated with iodine vapour, it loses oxygen: $\text{Na}_2\text{O}_2 + \text{I}_2 = \text{Na}_2\text{OI}_2 + \text{O}$. The compound Na_2OI_2 is akin to the compound Cu_2OCl_2 obtained by oxidising CuCl . This reaction is one of the few in which iodine directly displaces oxygen. The substance Na_2OI_2 is soluble in water, and when acidified gives free iodine and a sodium salt. Carbonic oxide is absorbed by heated sodium peroxide with formation of sodium carbonate, $\text{Na}_2\text{CO}_3(\text{Na}_2\text{O}_2 + \text{CO})$, whilst carbonic anhydride liberates oxygen from it. With nitrous oxide it reacts thus: $\text{Na}_2\text{O}_2 + 2\text{N}_2\text{O} = 2\text{NaNO}_2 + \text{N}_2$; with nitric oxide it combines directly, forming sodium nitrite, $\text{NaO} + \text{NO} = \text{NaNO}_2$. Sodium peroxide, when treated with water, does not give hydrogen peroxide, because the latter, in the presence of the alkali formed ($\text{Na}_2\text{O}_2 + 2\text{H}_2\text{O} = 2\text{NaHO} + \text{H}_2\text{O}_2$), decomposes into water and oxygen. In the presence of dilute sulphuric acid it forms H_2O_2 ($\text{Na}_2\text{O}_2 + \text{H}_2\text{SO}_4 = \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}_2$). The oxidising properties of Na_2O_2 under the action of heat are seen, for instance, in the fact that when heated with iodine it forms sodium iodate; with PbO , Na_2PbO_3 ; with pyrites, sulphates, &c. When peroxide of sodium comes into contact with water, it evolves much heat, forming H_2O_2 , and decomposing with the disengagement of oxygen; but, as a rule, there is no explosion. But if Na_2O_2 is placed in contact with organic matter, such as sawdust, cotton, &c., it gives a violent explosion when heated, ignited, or acted on by water. Peroxide of sodium forms an excellent oxidising agent for the preparation of the higher products of oxidation of Mn , Cr , W , &c., and also for oxidising the metallic sulphides.

Although the peroxide H_2O_2 is derived from hydrogen, and Na_2O_2 from sodium, yet there are no corresponding salts known, and if they are formed they are probably as unstable as hydrogen peroxide. Although carbon forms carbonic oxide, CO , still it has only one salt-forming oxide—carbonic anhydride, CO_2 . Nitrogen and chlorine both give several salt-forming oxides and types of salts. But of the oxides of nitrogen, NO and NO_2 do not form salts, as do N_2O_3 , N_2O_4 , and N_2O_5 , although N_2O_4 does not form special salts, and N_2O_5 corresponds with the highest form of the saline compounds of nitrogen. Such distinction between the elements, according to their power of giving one or several saline forms, is a radical property of no less importance than the basic or acid properties of their oxides. Sodium as a typical metal does not form any acid oxides, whilst chlorine, as a typical non-metal, does not form bases with oxygen. Therefore sodium *as an element* may be thus characterised: it forms one very stable salt-forming oxide, Na_2O , having powerful basic properties, and its salts are of the general formula NaX , so that in its compounds it is, like hydrogen, a basic and univalent element.

CHAPTER XIII

POTASSIUM, RUBIDIUM, CÆSIUM, AND LITHIUM. SPECTRUM ANALYSIS.

JUST as the series of halogens, fluorine, bromine, and iodine correspond with the chlorine contained in common salt, so also there exists a corresponding series of elements: lithium, $\text{Li} = 7$, potassium, $\text{K} = 39$, rubidium, $\text{Rb} = 85$, and cæsium, $\text{Cs} = 133$, which are analogous to the sodium in common salt. These elements bear as great a resemblance to sodium, $\text{Na} = 23$, as fluorine, $\text{F} = 19$, bromine, $\text{Br} = 80$, and iodine, $\text{I} = 127$, do to chlorine, $\text{Cl} = 35.5$. Indeed, in a free state, these elements, like sodium, are soft metals which rapidly oxidise in moist air and decompose water at the ordinary temperature, forming soluble hydroxides having clearly defined basic properties and the composition RHO , like that of caustic soda. The resemblance between these metals is sometimes seen with striking clearness, especially in compounds such as salts of the form MX .¹ The corresponding salts of nitric, sulphuric, carbonic, and nearly all acids with these metals have many points in

¹ Tutton's researches (1894) upon the analogy of the crystalline forms of K_2SO_4 , Rb_2SO_4 and Cs_2SO_4 may be taken as a typical example of the comparison of analogous compounds. We cite the following data from these excellent researches (which are still being continued): the sp. gr. at $20^\circ/4^\circ$ of K_2SO_4 is 2.6633, that of Rb_2SO_4 , 3.6113, and that of Cs_2SO_4 , 4.2434. The coefficient of cubical expansion (the mean between 20° and 60°) for the K salt is 0.0053, for the Rb salt 0.0052, and for the Cs salt 0.0051. The linear expansion (the maximum for the vertical axis) along the axis of crystallisation is the same for all three salts, within the limits of experimental error. The replacement of potassium by rubidium causes the distance between the centres of the molecules in the direction of the three axes of crystallisation to increase equally, and less than with the replacement of rubidium by cæsium. The index of refraction for all rays and for every crystalline path (direction) is greater for the rubidium salt than for the potassium salt, and less than for the cæsium salt. The lengths for the rhombic crystalline axes for K_2SO_4 are in the ratio 0.5727 : 1 : 0.7418; for Rb_2SO_4 , 0.5723 : 1 : 0.7485, and for Cs_2SO_4 , 0.5712 : 1 : 0.7521. The development of the basal and brachy-pinacoids gradually increases in passing from K to Rb and Cs. The optical properties also follow the same order, both at the ordinary and at a higher temperature. Tutton draws the general conclusion that the crystallographic properties of the isomorphic rhombic sulphates, R_2SO_4 , are a function of the atomic weights of the metals contained in them (see Chap. XV.). Such researches as these should do much towards hastening the establishment of a true molecular mechanics of physico-chemical phenomena, and also serve as a means of showing and expressing variable properties as a function of the atomic weights of the component elements.

common. These metals, which resemble sodium so much in their reactions, are termed the **metals of the alkalies**.

Among the metals of the alkalies, the most widely distributed in nature, after sodium, is **potassium**. Like sodium, it does not appear either in a free state or as oxide or hydroxide, but in the form of salts, which, in the manner of their occurrence, present much in common with those of sodium. The compounds of potassium and sodium in the earth's crust occur as mineral **compounds of silica**. With silica, SiO_2 , potassium oxide, like sodium oxide, forms saline mineral substances resembling glass. If other oxides, such as lime, CaO , and alumina, Al_2O_3 , combine with these compounds, glass is formed, a vitreous stony mass, distinguished by its great stability, and its very slight variation under the action of water. It is such complex silicious compounds as these containing potash (potassium oxide), K_2O , or soda (sodium oxide), Na_2O , and sometimes both together, silica, SiO_2 , lime, CaO , alumina, Al_2O_3 , and other oxides, that form the chief constituents of the rocks of which the greater portion of the accessible crust (envelope) of the earth is made up. The primary rocks, like granite, porphyry, &c., are composed of such crystalline silicious rocks as these. The oxides entering into the composition of these rocks do not form a homogeneous amorphous mass like glass, but are distributed in a series of peculiar, and in the majority of cases crystalline, compounds, into which the primary rocks may be divided. Thus a felspar (orthoclase) in granite contains from 8 to 15 per cent. of potassium, whilst another variety (plagioclase), which also occurs in granite, contains 1·2 to 6 per cent. of potassium, and 6 to 12 per cent. of sodium. The mica in granite contains 3 to 10 per cent. of potassium. As already mentioned, and further explained in Chap. XVII., the friable, crumbling, and stratified formations which cover the ocean-bed and a large part of the earth's surface have been formed from these primary rocks by the action of the atmosphere and of water containing carbonic acid. It is evident that in the chemical alteration of the primary rocks by the action of water, the compounds of potassium, as well as the compounds of sodium, must have been dissolved by the water (as they are soluble in water), and that therefore the compounds of potassium must be accumulated together with those of sodium in sea water. And indeed compounds of potassium are always found **in sea water**, as we have already pointed out (Chapters I. and X.). This forms one of the sources from which they are extracted. After the evaporation of sea water, there remains a mother liquor, which contains potassium chloride and a large proportion of magnesium chloride. On cooling this solution, crystals separate out which contain chlorides of

magnesium and potassium. A double salt of this kind, called **carnallite**, $\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$, occurs at Stassfurt. This carnallite² is now employed as a material for the extraction of potassium chloride, and of all the compounds of this element.³ Besides which, potassium chloride itself is sometimes found at Stassfurt as **sylvine**.^{3a} By methods of

² Carnallite belongs to those double salts which are directly decomposed by water, and it only crystallises from solutions which contain an excess of magnesium chloride. It may be prepared artificially by mixing strong solutions of potassium and magnesium chlorides, when colourless crystals of sp. gr. 1.60 separate, whilst the Stassfurt salt is usually of a reddish tint, owing to the presence of traces of iron. At the ordinary temperature sixty-five parts of carnallite are soluble in a hundred parts of water in the presence of an excess of salt. It deliquesces in the air, forming a solution of magnesium chloride and leaving potassium chloride. At the close of the nineteenth century the yearly production of salt at Stassfurt and in the neighbourhood was as follows: Carnallite, $\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$, 1,700,000 tons; karnite, $\text{K}_2\text{Mg}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, 1,200,000 tons; sylvine, KCl , 150,000 tons; or altogether about 3,000,000 tons of natural potassium salts a year. The greater part of this production is consumed by the agriculturist as manure, especially for beetroot. Van't Hoff studied all the conditions of the formation of all the Stassfurt salts from sea water.

³ The method of separating sodium chloride from potassium chloride has been described in Chapter I. On evaporation of a mixture of the saturated solutions, sodium chloride separates; then, on cooling, potassium chloride separates, owing to the difference of the rate of variation of their solubilities with the temperature. The following are the most trustworthy figures for the solubility of **potassium chloride** in one hundred parts of water (for sodium chloride, see Chap. X., note 13):—

10°	20°	40°	60°	100°
32	35	40	46	57

When mixed with solutions of other salts the solubility of potassium chloride naturally varies, but not to any great extent.

^{3a} The specific gravity of the solid salt is 1.99—that is, less than that of sodium chloride—so that it floats on the surface of liquids of sp. gr. 2.05 (which may easily be obtained from mixtures of the halogen derivatives of the hydrocarbons), while NaCl sinks to the bottom. All the salts of sodium are specifically heavier than the corresponding salts of potassium, as are also their solutions having equal percentage compositions. If the specific gravity of water at 4° is taken as 10,000, then at 15° the specific gravity of a solution of p per cent. of potassium chloride is given by $9,992 + 63.29p + 0.226p^2$, and is therefore, for 10 per cent., 1.0647, and for 20 per cent., 1.1348, &c.

Potassium chloride combines with iodine trichloride to form a compound $\text{KCl} + \text{ICl}_3 = \text{KICl}_4$, which has a yellow colour, is fusible, loses iodine trichloride at a red heat, and gives potassium iodate and hydrochloric acid with water. It is not only formed by direct combination, but also by many other methods; for instance, by passing chlorine into a solution of potassium iodide so long as the gas is absorbed, $\text{KI} + 2\text{Cl}_2 = \text{KCl} + \text{ICl}_3$. Potassium iodide, when treated with potassium chlorate and strong hydrochloric acid, also gives this compound; another method for its formation is given by the equation: $\text{KClO}_3 + \text{I} + 6\text{HCl} = \text{KCl} + \text{ICl}_3 + 3\text{Cl} + 3\text{H}_2\text{O}$. This salt corresponds with KIO_2 (unknown) in which the oxygen is replaced by chlorine. If valency be taken as the starting-point in the study of chemical compounds, and the elements considered as having a constant atomicity (number of bonds)—that is, if K, Cl, and I be taken as univalent elements—then it is impossible to explain the formation of such a compound because, according to this view, univalent elements are only able to form with each other dual compounds, such as KCl , ClI , KI , &c., whilst here they are grouped together in the molecule KICl_4 . Wells, Wheeler, and Penfield (1892), and subsequently others, obtained a large number

double saline decomposition, the chloride of potassium may be converted into all the other potassium salts,⁴ some of which are of practical use. The potassium salts have, however, their greatest importance as an indispensable component of the food of plants.⁵

The primary rocks contain an almost equal proportion of potassium and sodium. But in sea water the compounds of the latter metal predominate. It may be asked, What became of the compounds of potassium in the disintegration of the primary rocks if so small a quantity went to the sea water? They remained with the other solid products of the decomposition of the primary rocks. When granite or any other similar rock formation is disintegrated, it yields, besides the soluble substances, mainly (insoluble) sand and finely divided clay, containing water, alumina, and silica. This clay is carried away by the water, and is then deposited in strata. It retains, and especially when mixed with vegetable remains, compounds of potassium in greater quantity than

of such poly-haloid salts. They may all be divided into two large classes, the tri-haloid and the penta-haloid salts. They have been obtained not only for K but also for Rb and Cs, and to some extent also for Na and Li. The general method of their formation consists in dissolving the ordinary halogen salt of the metal in water, and treating it with the requisite amount of free halogen. The poly-haloid salt separates out after evaporating the solution at a more or less low temperature. In this manner, among the tri-haloid salts, may be obtained: KI_3 , KBr_2I , KCl_2I , and the corresponding salts of rubidium and caesium; for instance, CsI_3 , CsBrI_2 , CsBr_2I , CsClBrI , CsCl_2I , CsBr_3 , CsClBr_2 , CsCl_2Br , and in general MX_3 , where X is a halogen. The colour of the crystals varies according to the halogen; thus CsI_3 is black, CrBr_3 yellowish red, CsBrI_2 reddish brown, CsBr_2I red, and CsCl_2Br yellow. The caesium salts are the most stable, and those of potassium the least so. The penta-haloid salts form a smaller class; of such salts potassium forms KCl_4I , rubidium RbCl_4I , caesium CsI_5 , CsBr , CsCl_4I , lithium LiCl_4I (with $4\text{H}_2\text{O}$), and sodium NaCl_4I (with $2\text{H}_2\text{O}$). The most stable are those salts containing the metal with the greatest atomic weight—caesium (see Chap. XI., note 63).

⁴ It is possible to extract the compounds of potassium directly from the primary rocks which are so widely distributed over the earth's surface and are so abundant in certain localities. From a chemical point of view this problem presents no difficulty; for instance, by fusing powdered orthoclase with lime and fluor spar (Ward's method) and then extracting the alkali with water (on fusion the silica gives an insoluble compound with lime), or by treating the orthoclase with hydrofluoric acid (in which case silicon fluoride is evolved as a gas), it is possible to transfer the alkali of the orthoclase to an aqueous solution, and to separate it in this manner from the insoluble oxides. However, as yet there is no profit in, nor necessity for, recourse to this treatment, as carnallite and potash form abundant materials for the extraction of potassium compounds by cheaper methods. Furthermore, the salts of potassium are now, in the majority of chemical reactions, replaced by salts of sodium. The replacement of potassium compounds by sodium compounds not only has the advantage that the salts of sodium are in general the cheaper, but also that, for a given reaction, a smaller quantity of a sodium salt is needed, because the combining weight of sodium (23) is less than that of potassium (39).

⁵ It has been shown, by direct experiment on the cultivation of plants in artificial soils and in solutions, that under conditions (physical, chemical, and physiological) otherwise identical, plants are able to thrive and become fully developed in the entire absence of sodium salts, but that their development is impossible without potassium salts.

those of sodium. This has been proved with absolute certainty to be the case, and is due to the **absorptive power of the soil**. If a dilute solution of a potassium compound be filtered through common mould used for growing plants, containing clay and the remains of vegetable decomposition, the mould will be found to have retained a somewhat considerable percentage of the potassium compounds. If a salt of potassium be taken, then, during the filtration, an equivalent quantity of a calcium salt—also found, as a rule, in soils—is set free. Such a process of filtration through the soil proceeds in nature, and the compounds of potassium are everywhere retained by the friable earth in considerable quantity. This explains the presence of so small an amount of potassium salts in the water of rivers, lakes, streams, and oceans, where the lime, soda, and magnesia have accumulated. The compounds of potassium retained by the friable mass of the earth are absorbed as an aqueous solution by the roots of **plants**. As everyone knows, plants when burnt leave an ash, and this ash, besides various other substances, always contains compounds of potassium. Many land plants contain a very small amount of sodium compounds,⁶ whilst potassium and its compounds occur in all kinds of vegetable ash. Among the generally cultivated plants, grass, potatoes, the turnip, and buckwheat are particularly rich in potassium compounds. The ash of plants, and especially of herbaceous plants, buckwheat straw, sunflower and potato leaves are used in practice for the extraction of potassium compounds. There is no doubt that potassium occurs in the plants themselves in the form of complex compounds, and often as salts of organic acids. In certain cases such salts of potassium are even extracted from the juice of plants. Thus, sorrel and oxalis, for example, contain in their juices the acid oxalate of potassium, C_2HKO_4 , which is employed for removing ink-stains. Grape juice contains the so-called cream of tartar, which is the acid tartrate of potassium, $C_4H_5KO_6$.⁷

⁶ If herbaceous plants contain much sodium salts, it is evident that these salts mainly come from the sodium compounds in the water absorbed by the plants.

⁷ As plants always contain mineral substances and cannot thrive in a medium which does not contain them, more especially in one which is free from the salts of the four basic oxides, K_2O , CaO , MgO , and Fe_2O_3 , and of the four acid oxides, CO_2 , N_2O_5 , P_2O_5 , and SO_3 , and as the amount of ash-forming substances in plants is small, the question inevitably arises as to what part these play in the development of plants. With the existing chemical data only one answer is possible to this question, and it is still only an hypothesis. This answer was particularly clearly expressed by Professor Gustavson, of the Petroffsky Agricultural Academy. Starting from the fact (Chap. XI., note 55) that a small quantity of aluminium renders possible or facilitates the reaction of bromine on hydrocarbons at the ordinary temperature, it is easy to arrive at the conclusion, which is very probable and in accordance with many data respecting the reactions of organic compounds, that the addition of mineral substances to organic compounds lowers the temperature of reaction, and in general facilitates chemical reactions in plants, thus

This salt also separates as a sediment from wine. When the plants, containing one or more of the salts of potassium, are burnt, the carbonaceous matter is oxidised, and in consequence the potassium is obtained in the ash as carbonate, K_2CO_3 , which is generally known as **potashes**. Hence potashes occur ready prepared in the ash of plants (like soda in the ash of seaweeds), and therefore the ash of land plants is employed as a source for the extraction of potassium compounds. Potassium carbonate is extracted by lixiviating the ash with water.⁸ Potassium carbonate may also be obtained from

aiding the conversion of the most simple nourishing substances into the complex component parts of the plant organism. The province of chemical reactions proceeding in organic substances in the presence of a small quantity of mineral substances has as yet been but little investigated, although there are already several disconnected data concerning reactions of this kind, and although a great deal is known with regard to such reactions among inorganic compounds. The essence of the matter may be expressed thus—two substances, A and B, do not react on each other of their own accord, but the addition of a small quantity of a third particularly active substance, C, produces the reaction of A on B, because A combines with C, forming AC, and B reacts on this new compound, which has a different store of chemical energy, forming the compound AB or its products, and either setting C free again or retaining it.

It may here be remarked that all the mineral substances necessary for plants (those enumerated at the beginning of the note) are the highest saline compounds of their elements, that they enter into the plants as salts, that the lower forms of oxidation of the same elements (for instance, sulphites and phosphites) are harmful to plants (poisonous), and that strong solutions of the salts assimilated by plants not only do not enter into the plants but kill them (poison them).

Besides which, it will be understood from the preceding paragraph that the salts of potassium may become exhausted from the soil by long cultivation, and that there may therefore be cases when direct fertilisation by salts of potassium may be profitable. But manure and animal excrements, ashes, and, in general, nearly all refuse which may serve for fertilising the soil, contain a considerable quantity of potassium salts, and therefore, as regards natural salts of potassium (Stassfurt), and especially potassium sulphate, if they often improve the crops, it is in all probability due to their action on the properties of the soil. The agriculturist cannot therefore be advised to add potassium salts, without making special experiments showing the advantage of such a fertiliser on a given kind of soil and plant.

⁸ The animal body also contains potassium compounds, as would be expected, seeing that animals consume plants. For example, milk, and especially human milk, contains a considerable quantity of potassium compounds. Cow's milk, however, does not contain much potassium salt. Sodium compounds generally predominate in the bodies of animals. The excrements of animals, and especially of herbivorous animals, on the contrary, often contain a large proportion of potassium salts. Thus sheep's dung is rich in them, and in washing sheep's wool salts of potassium pass into the water.

The ash of tree stems, as the already dormant portion of the plant (Chap. VIII., note 1), contains little potash. For the extraction of potash, which was formerly carried on extensively in the east of Russia (before the discovery of the Stassfurt salt), the ash of grasses, and the green portions of potatoes, buckwheat, &c., are taken and treated with water (lixivated), the solution evaporated, and the residue ignited in order to destroy the organic matter present in the extract. The residue thus obtained is composed of raw potash. It is refined by a second dissolution in a small quantity of water. The solution thus obtained is again evaporated, and the residue ignited, and this potash is then called refined potash, or pearlash. This method of treatment cannot give

the chloride by a method similar to that by which sodium carbonate is prepared from sodium chloride. There is no difficulty in obtaining any salt of potassium—for example, the sulphate,⁹ bromide, and

chemically pure potassium carbonate. To obtain chemically **pure potassium carbonate**, some other salt of potassium is generally taken and purified by crystallisation. Potassium carbonate crystallises with difficulty, and it cannot therefore be purified by this means, whilst other salts, such as the tartrate, acid carbonate, sulphate, nitrate, &c., crystallise easily, and may thus be directly purified. The tartrate is most frequently employed, since it is prepared in large quantities (as a sediment from wine) for medicinal use under the name of cream of tartar. When ignited without access of air, it leaves a mixture of charcoal and potassium carbonate. The charcoal so obtained being in a finely divided condition, the mixture (called 'black flux') is sometimes used for reducing metals from their oxides with the aid of heat. A certain quantity of nitre is added to burn the charcoal formed by heating the cream of tartar. Potassium carbonate thus prepared is further purified by converting it into the acid salt, by passing a current of carbonic anhydride through a strong solution. KHCO_3 is then formed, which is less soluble than the normal salt (as is also the case with the corresponding sodium salt), and therefore crystals of the acid salt separate out on cooling. When ignited, they part with their water and carbonic anhydride, and pure potassium carbonate remains behind. The physical properties of potassium carbonate are sufficient to distinguish it clearly from sodium carbonate; it is obtained from solution as a powdery white mass, having an alkaline taste and reaction, and, as a rule, shows only traces of crystallisation. It also attracts the moisture of the air with great energy. The crystals do not contain water, but absorb it from the air, deliquescent into a saturated solution. It melts at a red heat (1045°), and at a still higher temperature is even converted into vapour, as has been observed at glass works where it is employed. It is very soluble, and at the ordinary temperature, water dissolves an equal weight of the salt. Crystals containing two equivalents of water separate from such a saturated solution when strongly cooled (Morel obtained $\text{K}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}$ in well-formed crystals at $+10^\circ$). Its reactions are all analogous to those of sodium carbonate. When manufactured sodium carbonate was but little known, the consumption of potassium carbonate was very considerable, and even now washing soda is frequently replaced for household purposes by **ley**—i.e., an aqueous solution obtained from ashes—which acts like soda.

A mixture of potassium and sodium carbonates fuses with much greater ease than the separate salts, and a mixture of their solutions gives well-crystallised salts—for instance (Marguerite's salt), $\text{K}_2\text{CO}_3 \cdot 6\text{H}_2\text{O} \cdot 2\text{Na}_2\text{CO}_3 \cdot 6\text{H}_2\text{O}$. Crystallisation also occurs with other relative proportions of K and Na (in the above case 1 : 2, but 1 : 1 and 1 : 3 are known), and always with 6 mol. H_2O . This is evidently a combination *by similarity*, as in alloys, solutions, &c.

⁹ **Potassium sulphate**, K_2SO_4 , crystallises from its solutions in an anhydrous condition, in which respect it differs from the corresponding sodium salt, just as potassium carbonate differs from sodium carbonate. In general, it must be observed that the majority of sodium salts combine more easily with water of crystallisation than those of potassium. The solubility of potassium sulphate does not show the same peculiarities as that of sodium sulphate, because it does not combine with water of crystallisation; at the ordinary temperature 100 parts of water dissolve about 10 parts of the salt, at 0° 8.3 parts, and at 100° about 26 parts. The **acid sulphate**, KHSO_4 , readily obtainable by heating crystals of the normal salt with sulphuric acid, is frequently employed in chemical practice. On heating the mixture of acid and salt, fumes of sulphuric acid are at first given off; when they cease to be evolved, the acid salt is contained in the residue. At a higher temperature (above 600°) the acid salt parts with the acid contained in it, the normal salt being re-formed. The definite composition of this acid salt and the ease with which it decomposes render it exceedingly valuable for certain chemical transformations accomplished by means of sulphuric acid at a high temperature, because it is possible

iodide¹⁰—by the action of the corresponding acid on KCl and especially on the carbonate, whilst the hydroxide, **caustic potash**, KHO, which is in many respects analogous to caustic soda, is easily obtained by means of lime¹¹ or by the action of an electric current on a solution of KCl (about 2 kilo-watt hours are consumed per 1 kilo of KHO). Therefore, in order to complete our knowledge of the alkali metals, we will only

to take, in the form of this salt, a definite quantity of sulphuric acid, and to cause it to act on a given substance at a high temperature. In this case, the acid salt acts in the same manner as sulphuric acid itself. The acid potassium sulphate is employed, where for conversion of certain oxides, such as those of iron, aluminium, and chromium, into salts, a high temperature is required.

¹⁰ The **bromide** and **iodide of potassium** are used, like the corresponding sodium compounds, in medicine and photography. Potassium iodide is obtained by saturating a solution of hydriodic acid with caustic potash. In practice, however, it is prepared by the direct formation of hydriodic acid in solution in the presence of potassium hydroxide or carbonate. Thus iodine is thrown into a solution of pure potash, and hydrogen sulphide passed through the mixture, the iodine being thus converted into hydriodic acid. Or a solution is prepared from phosphorus, iodine, and water, containing hydriodic and phosphoric acids; lime is then added to this solution, when calcium iodide is obtained in solution, and calcium phosphate as a precipitate. The solution of calcium iodide gives, with potassium carbonate, insoluble calcium carbonate and a solution of potassium iodide. If iodine is added to a slightly heated solution of caustic potash (free from carbonate—that is, freshly prepared), so long as the solution is not coloured from the presence of an excess of iodine, there is formed a mixture of potassium iodide and iodate. On evaporating the solution thus obtained and igniting the residue, the iodate is destroyed and converted into potassium iodide. On dissolving the residue in water and then evaporating, cubical crystals (like NaCl) of the anhydrous salt are obtained, which are soluble in water and alcohol, and on fusion give an alkaline reaction, owing to the fact that when ignited a portion of the salt decomposes, forming potassium oxide. The neutral salt may be obtained by adding hydriodic acid to this alkaline salt until it gives an acid reaction. It is best to add some finely divided charcoal to the mixture of iodate and iodide before igniting it, as this facilitates the evolution of the oxygen from the iodate. Potassium iodide may also be prepared by mixing a solution of ferrous iodide (it is best if the solution contains an excess of iodine) and potassium carbonate, in which case ferrous carbonate, FeCO_3 , is precipitated (with an excess of iodine the precipitate is granular, and contains a compound of the suboxide and oxide of iron), whilst potassium iodide remains in solution. Ferrous iodide, FeI_2 , is obtained by the direct action of iodine on iron in water. Potassium iodide considerably lowers the temperature (by 24°), when it dissolves in water; 100 parts of the salt dissolve in 73.5 parts of water at 12.5° or in 70 parts at 18° , whilst the saturated solution, which boils at 120° , contains 100 parts of salt per 45 parts of water. Solutions of potassium iodide dissolve a considerable amount of iodine, strong solutions dissolving even as much or more iodine than they contain as potassium iodide (see note 3a, and Chap. XI., note 64).

¹¹ Caustic potash is also formed by igniting potassium nitrate with finely divided copper (see note 15), and also by mixing solutions of potassium sulphate (or even of alum, KAlS_2O_8) and barium hydroxide, BaH_2O_2 . It is sometimes purified by dissolving it in alcohol (the impurities, for example, potassium sulphate and carbonate, are not dissolved) and then evaporating the alcohol.

The specific gravity of potassium hydroxide is 2.04, but that of its solutions (see Chap. XII., note 18) at 15° is expressed by $S = 9.992 + 90.4p + 0.28p^2$. Strong solutions, when cooled, yield a crystallo-hydrate, $\text{KHO} \cdot 4\text{H}_2\text{O}$, which dissolves in water, producing cold (like $2\text{NaHO} \cdot 7\text{H}_2\text{O}$), whilst potassium hydroxide in solution develops a considerable amount of heat.

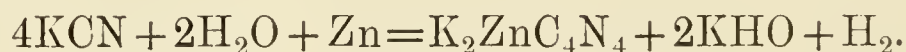
describe two salts of potassium which are of practical importance, and whose analogues have not been described in the preceding chapter, namely, potassium cyanide and potassium nitrate.

Potassium cyanide, which presents in its chemical and physical^{11a} relations a certain analogy with the halogen salts of potassium, is not only formed according to the equation, $\text{KHO} + \text{HCN} = \text{H}_2\text{O} + \text{KCN}$, but also whenever a nitrogenous carbon compound—for instance, animal matter—is heated in the presence of metallic potassium, or of a compound of potassium, and even when a mixture of potash and carbon is heated in a stream of nitrogen. Potassium cyanide is obtained from yellow prussiate of potash, which has been already mentioned in Chapter IX., and the preparation of which on a large scale will be described in Chapter XXII. If the yellow prussiate is ground to a powder and dried, so that it loses its water of crystallisation, it then melts at a red heat, decomposing into carbide of iron, nitrogen, and potassium cyanide, $\text{FeK}_4\text{C}_6\text{N}_6 = 4\text{KCN} + \text{FeC}_2 + \text{N}_2$. After the decomposition it is found that the yellow salt has been converted into a white mass of potassium cyanide. The carbide of iron formed collects at the bottom of the vessel. If the mass thus obtained is treated with water, the potassium cyanide is partially decomposed by the water, but if it is treated with alcohol, the cyanide is dissolved, and on cooling separates in a crystalline form.¹² If the yellow prussiate is heated with potassium, it deposits all its iron and is converted into potassium

^{11a} Thus, for instance, KCN crystallises in cubes like KCl.

¹² When the yellow prussiate is heated to redness, all the cyanogen which was in combination with the iron is decomposed into nitrogen, which is evolved as gas, and carbon, which combines with the iron. In order to avoid this, potassium carbonate is added to the yellow prussiate while it is being fused. A mixture of 8 parts of anhydrous yellow prussiate and 3 parts of pure potassium carbonate is generally taken. Double decomposition then takes place, resulting in the formation of ferrous carbonate and potassium cyanide. But by this method a pure salt is not obtained, because a portion of it is oxidised and forms potassium cyanate, KCNO. By adding one part of charcoal powder to the mixture of 8 parts of anhydrous yellow prussiate and 3 parts of potassium carbonate, a mass is obtained which is free from cyanate, but in that case it is impossible to obtain a colourless salt by simple fusion, although this may easily be done by dissolving it in alcohol. Cyanide of potassium may also be obtained from potassium thiocyanate, which is formed from ammonium thiocyanate obtained by the action of ammonia upon bisulphide of carbon (see works upon organic chemistry). Potassium and sodium cyanides are now prepared in large quantities from yellow prussiate for the extraction of gold (Chap. XXIV.) and for gilding and silver-plating. KCN and NaCN are prepared by heating powdered and dried yellow prussiate with metallic sodium: $\text{K}_4\text{Fe}(\text{CN})_6 + 2\text{Na} = 4\text{KCN} + 2\text{NaCN} + \text{Fe}$. This method (Rossler and Gesslaker) offers two advantages over the above methods: (1) the whole of the cyanide is obtained in a combined state and does not decompose with the formation of N_2 and C_2 , and (2) no cyanates are formed, as is the case when carbonate of potash is heated with the prussiate. Pure KCN is obtained by passing CNH into an alcoholic solution of KHO.

cyanide, $\text{K}_4\text{Fe}(\text{CN})_6 + 2\text{K} = 6\text{KCN} + \text{Fe}$. A solution of potassium cyanide has a powerfully alkaline reaction, a smell like that of bitter almonds, peculiar to prussic acid, and acts as a most powerful poison. Although exceedingly stable in a fused state, potassium cyanide easily changes when in solution. Prussic acid is so very feebly energetic that water gives a certain amount of KHO with potassium cyanide. A solution of the salt, even at a low temperature, quickly turns brown and decomposes, and when heated evolves ammonia and forms potassium formate; this is easily comprehensible from the representation of the cyanogen compounds which was developed in Chapter IX., $\text{KCN} + 2\text{H}_2\text{O} = \text{CHKO}_2 + \text{NH}_3$. Furthermore, as carbonic anhydride acts on potassium cyanide with evolution of prussic acid, and as potassium cyanate, which is also unstable, is formed by the action of air, it will easily be seen that solutions of potassium cyanide are very unstable. Potassium cyanide, containing as it does carbon and potassium, is a substance which can exert a very vigorous reducing action, especially when fused; it is therefore used as a powerful reducing agent at a red heat.¹³ The property of potassium cyanide of giving double salts with other cyanides is very clearly shown by the fact that many metals dissolve in a solution of potassium cyanide, with the evolution of hydrogen. For example, iron, copper, and zinc act in this manner. Thus—



Gold and silver are soluble in potassium cyanide in the presence of air, in which case the hydrogen, which would otherwise be evolved in the reaction, combines with the oxygen of the air, forming water (Eissler, MacLaurin, 1893), for example, $4\text{Au} + 4\text{KCN} + \text{O} + \text{H}_2\text{O} = 2\text{AuKC}_2\text{N}_2 + 2\text{KHO}$, which is taken advantage of for extracting gold from its ores (Chap. XXIV.).^{13a} Platinum, mercury, and tin are not dissolved in a solution of potassium cyanide, even with access of air. The sodium salt acts in the same manner.

Potassium nitrate, or common nitre or saltpetre, KNO_3 , is chiefly used as a component part of ordinary black gunpowder, in which it cannot be replaced by the sodium salt, because the latter is deliquescent.

¹³ A considerable quantity of potassium cyanide is used in the arts, more particularly for the preparation of metallic solutions employed in electro-silvering and gilding. An alkaline solution is prepared, which is moderately stable owing to the fact that in the form of certain double salts—that is, combined with other cyanides—potassium cyanide is far more stable than when alone.

^{13a} A dilute solution of KCN is taken, containing not more than 1 per cent. of KCN. MacLaurin states that such solutions dissolve more air (than strong ones), the oxygen of which is necessary for the reaction (see Chap. XXIV., note 30).

The nitre in gunpowder should therefore be perfectly pure, as even small traces of sodium, magnesium, and calcium salts, especially chlorides, render the nitre and the gunpowder capable of attracting moisture. Nitre may easily be obtained pure, owing to its great disposition to form crystals, which aids its separation from other salts. The considerable differences between the solubilities of nitre at different temperatures help this crystallisation. A solution of nitre saturated at its boiling-point (116°) contains 335 parts of nitre to 100 parts of water, whilst at the ordinary temperature—for instance, 20° —the solution is only able to retain 32 parts of the salt. Therefore, in the preparation and refining of nitre, its solution, saturated at the boiling-point, is cooled, and nearly all the nitre is obtained in the form of crystals. If the solution is quietly and slowly cooled in large quantities, large crystals are formed; but if it is rapidly cooled, so as to prevent the formation of large crystals (in the crevices of which the mother liquor, together with the impurities, would remain), the very minute crystals of nitre known as saltpetre flour are obtained, and this is the usual method adopted for crystallising nitre.

Common nitre occurs in nature, but only in small quantities in admixture with other nitrates, especially those of sodium, magnesium, and calcium. Such a mixture of salts of nitric acid is formed in those localities, where, as in **the soil**, nitrogenous organic remains are decomposed in the presence of alkalies or alkaline bases with free access of air. This method of the formation of nitrates requires moisture, besides the free access of air, and takes place principally during warm weather.¹⁴ In warm countries, and in temperate climates during the summer months, fertile soils produce a small quantity of nitre. In this respect India is especially known as affording a considerable supply of nitre extracted from the soil. The nitre-bearing soil after the rainy season sometimes becomes covered during the summer with crystals of nitre, formed by the evaporation of the water in which it was previously dissolved. This soil is collected, subjected to repeated lixiviations, and treated for nitre in the way to be presently described. In temperate climates nitrates are obtained from the **lime rubbish** of demolished buildings which have stood for many years, and especially from those portions which have been in contact with the ground.

¹⁴ Besides which, Schloëssing and Müntz, by employing similar methods to Pasteur, showed that the formation of nitre in the decomposition of nitrogenous substances is accomplished by the aid of peculiar micro-organisms (ferments), without which the simultaneous action of the other necessary conditions (alkalies, moisture, a temperature of 37° , air, and nitrogenous substances) cannot give nitre. The addition of colonies of these organisms facilitates the rapid formation of nitre. The organisms occur in the atmosphere.

The conditions there are very favourable for the formation of nitre, because the lime used as a cement in buildings contains the base necessary for the formation of nitrates, while excrements, urine, and animal refuse are sources of nitrogen. By the methodical lixiviation of this kind of rubbish a solution of nitrogenous salts is formed similar to that obtained by the lixiviation of fertile soil. A similar solution is also obtained by the lixiviation of the so-called **nitre plantations**. These are composed of manure interlaid with brushwood, and strewn over with ashes, lime, and other alkaline rubbish. These nitre plantations are set up in localities where the manure is not required for the fertilisation of the soil, as, for example, in the south-eastern 'black earth' governments of Russia. The same process of oxidation of nitrogenous matter freely exposed, during the warm season, to air and moisture in the presence of alkalies takes place in nitre plantations as occurs in fertile soil and in the walls of buildings. From all these sources there is obtained a solution containing various salts of nitric acid mixed with soluble organic matter. The simplest method of treating this impure solution of nitre is to add a solution of potassium carbonate, or to simply treat it with ashes containing this substance. The potassium carbonate enters into double decomposition with the calcium and magnesium salts, forming insoluble carbonates of these bases and leaving the nitre in solution. Thus, for instance, $K_2CO_3 + Ca(NO_3)_2 = 2KNO_3 + CaCO_3$. Both calcium and magnesium carbonates are insoluble, and therefore after treatment with potassium carbonate the solution contains only the salts of sodium and potassium together with organic matter. The latter partially separates in an insoluble form on heating, and is entirely destroyed by heating the nitre to a low red heat. The nitre thus obtained is easily purified by repeated crystallisation. The greater part of the nitre used for making ordinary gunpowder is now obtained from the sodium salt, **Chili saltpetre** or **cubic nitre**, which occurs in nature, as already mentioned. The conversion of this salt into common nitre is also carried on by adding potassium carbonate (when, on mixing the strong and hot solutions, sodium carbonate is directly obtained as a precipitate), or, as is now most frequent, potassium chloride. When a mixture of strong solutions of potassium chloride and sodium nitrate is evaporated, sodium chloride first separates, because this salt, which is formed by the double decomposition, $KCl + NaNO_3 = KNO_3 + NaCl$, is almost equally soluble in hot and cold water; on cooling, therefore, a large amount of potassium nitrate separates from the saturated solution, while the sodium chloride remains dissolved. The nitre is ultimately purified by recrystallisation and by washing with a saturated solution

of nitre, which cannot dissolve a further quantity of nitre, but only the impurities.

Nitre is a colourless salt having a peculiar cool taste. It crystallises easily in long striated six-sided rhombic prisms terminating in rhombic pyramids. Its crystals (sp. gr. 1.93) do not contain water. At a low red heat (339°) nitre melts to a colourless liquid.^{14a} Potassium nitrate at the ordinary temperature and in a solid form is inactive and stable, but **at a high temperature** it acts as a powerful **oxidising agent**, giving up a considerable amount of oxygen to substances mixed with it.¹⁵ When thrown on to incandescent charcoal it brings about its rapid combustion, and a mechanical mixture of powdered charcoal and nitre ignites when brought into contact with a red-hot substance, and continues to burn by itself. In this action, nitrogen is evolved, and the oxygen oxidises the charcoal, in consequence of which potassium carbonate and carbonic anhydride are formed: $4\text{KNO}_3 + 5\text{C} = 2\text{K}_2\text{CO}_3 + 3\text{CO}_2 + 2\text{N}_2$. This phenomenon depends on the fact that oxygen in combining with carbon evolves more heat than it does in combining with nitrogen. Hence, when once the combustion has been started at the expense of the nitre, it is able to go on without the aid of external heat. A similar oxidation or combustion at the expense of the contained oxygen takes place when nitre is heated with different combustible substances. For

^{14a} Before fusing, the crystals of potassium nitrate change their form, and take the same form as sodium nitrate—that is, they change into rhombohedra. Nitre crystallises from hot solutions, and in general under the influence of a rise of temperature, in a different form from that given at the ordinary or lower temperatures. Fused nitre solidifies to a radiated crystalline mass; but it does not exhibit this structure if metallic chlorides are present, so that this method may be taken advantage of to determine the degree of purity of nitre.

Carnelley and Thomson (1888) determined the fusing-point of mixtures of potassium and sodium nitrates. The first salt fuses at 339° and the second at 316° , and if p is the percentage amount of potassium nitrate, the results obtained are—

$p = 10$	20	30	40	50	60	70	80	90
298°	283°	268°	242°	231°	231°	242°	284°	306°

A somewhat similar result was arrived at by the same observers for the solubility of mixtures of these salts in 100 parts of water at 20° . Thus, if p be the weight of potassium nitrate mixed with $100 - p$ parts by weight of sodium nitrate taken for solution, and c be the quantity of the mixed salts which dissolves in 100—the solubility of sodium nitrate being 85, and that of potassium nitrate 34, parts—parts of water, then—

$p = 10$	20	30	40	50	60	70	80	90
$c = 110$	136	136	138	106	81	73	54	41

It is instructive to note that the maximum solubility does not correspond with the minimum fusing-point, which naturally depends on the fact that in solution a third substance, namely water, plays a part (see note 8).

¹⁵ Fused nitre, with a further rise of temperature, disengages oxygen and then nitrogen. The nitrite, KNO_2 , is first formed, and then potassium oxide. The admixture of certain metals—for example, finely divided copper—aids the last decomposition. The oxygen in this case naturally passes over to the metal.

instance, $2\text{KNO}_3 + 2\text{S} = \text{K}_2\text{SO}_4 + \text{N}_2 + \text{SO}_2$. The oxidation of those metals which are able to form acid oxides with an excess of oxygen is especially remarkable. In this case they remain in combination with potassium oxide as potassium salts. Manganese, antimony, arsenic, iron, chromium, &c., are instances of this kind. These elements, like carbon and sulphur, displace free nitrogen. The lower oxides of these metals when fused with nitre pass into the higher oxides. It will be readily understood from this that nitre is frequently used in practical chemistry and the arts as an oxidising agent at high temperatures, its application in **gunpowder** is based on this property. Gunpowder consists of a mechanical mixture of finely ground sulphur, nitre, and charcoal. The relative proportions of these substances vary according to the requirements of the powder and to the kind of charcoal employed (a friable, incompletely burnt charcoal, containing therefore hydrogen and oxygen, is employed). Gases are formed in its combustion, chiefly nitrogen and carbonic anhydride, which create a considerable pressure if their escape be in any way impeded. This action of gunpowder may be expressed by the equation: $2\text{KNO}_3 + 3\text{C} + \text{S} = \text{K}_2\text{S} + 3\text{CO}_2 + \text{N}_2$.

It is found by this equation that gunpowder should contain thirty-six parts of charcoal (13·3 per cent.) and thirty-two parts (11·9 per cent.) of sulphur to 202 parts (74·8 per cent.) of nitre, which is very near to its actual composition.¹⁶

¹⁶ In China, where the manufacture of gunpowder has long been carried on, 75·7 parts of nitre, 14·4 of charcoal, and 9·9 of sulphur were used. Ordinary powder for sporting purposes contains 80 parts of nitre, 12 of charcoal, and 8 of sulphur, whilst the gunpowder used in heavy ordnance contains 75 of nitre, 15 of charcoal, and 10 of sulphur. Gunpowder explodes when heated to 300° , when struck, or on contact with a spark. A compact or finely divided mass of gunpowder burns slowly and has but little disruptive action, because it burns gradually from layer to layer. To act properly the gunpowder must have a definite rate of combustion, so that the pressure should increase during the passage of the projectile along the barrel of the fire-arm. This is done by making the powder in large granules or in the shape of six-sided prisms with holes through them (prismatic powder).

The products of combustion are of two kinds: (1) gases which produce the pressure and are the cause of the dynamical action of gunpowder, and (2) a solid residue, usually of a black colour owing to its containing unburnt particles of charcoal. Besides charcoal, the residue generally contains potassium sulphide, K_2S , and a whole series of other salts—for instance, carbonate and sulphate. It is apparent from this that the combustion of gunpowder is not so simple as it appears to be from the above equation, and hence the weight of the residue is also greater than the calculated. According to the equation, 270 parts of gunpowder give 110 parts of residue—that is, 100 parts of powder give 37·4 parts of residue, K_2S , whilst in reality the weight of the residue varies from 40 to 70 per cent. (generally 52 per cent.). This difference depends on the fact that so much oxygen (of the nitre) remains in the residue, and it is evident that if the residue varies the composition of the gases evolved by the powder will vary also, and therefore the entire process will be different in different cases. The difference in the composition of the gases and residue depends, as the researches of Gay-Lussac, Shishkoff and Bunsen, Nobel and Abel, Federoff, Debus, &c., show, on the conditions under which the

Metallic potassium was obtained like sodium ; first by the action of a galvanic current, then by reduction of the hydroxide by means of metallic iron, and lastly by the action of charcoal and carbide of iron on the carbonate at a high temperature, or on caustic potash (also Fe on K_2S). The preparation of **metallic potassium** with the aid of charcoal differs, however, from that of sodium, because it easily combines with carbonic oxide, forming an explosive and inflammable mass.¹⁷

Potassium is more volatile than sodium. At the ordinary temperature potassium is softer than sodium ; its freshly cut surface presents a whiter colour than that of sodium, and, like the latter, and even with greater ease, it oxidises in moist air. It is brittle at low temperatures, but is quite soft at 25° , and melts at about 60° . At a low red heat (667° , Perkin) it distils without change, forming a green vapour, whose density,¹⁸ according to A. Scott (1887), is equal to 19 (that of hydrogen

combustion of the powder proceeds. When gunpowder burns in an open space, the gaseous products formed do not remain in contact with the residue, and a considerable portion of the charcoal entering into the composition of the powder remains unburnt, because the charcoal burns after the sulphur at the expense of the oxygen of the nitre. In this extreme case the *commencement* of the combustion of the gunpowder may be expressed by the equation, $2KNO_3 + 3C + S = 2C + K_2SO_4 + CO_2 + N_2$. The residue in a blank cartridge often consists of a mixture of C, K_2SO_4 , K_2CO_3 , and $K_2S_2O_3$. If the combustion of the gunpowder be impeded—if it take place in a cartridge in the barrel of a gun—the quantity of potassium sulphate will first be diminished, then the amount of sulphite, whilst the amount of carbonic anhydride in the gases and the amount of potassium sulphide in the residue will increase. The quantity of charcoal entering into the action will then be also increased, and hence the amount in the residue will decrease. Under these circumstances the weight of the residue will be less—for example, $4K_2CO_3 + 4S = K_2SO_4 + 3K_2S + 4CO_2$. Besides which, carbonic oxide has been found in the gases, and potassium bisulphide, K_2S_2 , in the residue of gunpowder. The amount of potassium sulphide, K_2S , increases with the completeness of the combustion ; it is formed in the residue at the expense of the potassium sulphite. In recent times the knowledge of the action of gunpowder and other explosives has made much progress, and has developed into a vast province of artillery science, which, guided by the discoveries of chemistry, has worked out a ‘smokeless powder’ which burns without leaving a residue, and does not therefore give any ‘powder smoke’ (to hinder the rapidity of firing and aiming), and at the same time disengages a greater volume of gas and consequently gives (under proper conditions of combustion) the possibility of communicating to the charge a greater initial velocity, and therefore greater range, force, and accuracy of aim (Chap. VI., note 37).

¹⁷ The substances obtained in this case are mentioned in Chap. IX., note 31.

¹⁸ A. Scott (1887) determined the vapour densities of many of the alkali elements and of their compounds in a platinum vessel heated in a furnace and previously filled with nitrogen. Taking the density of hydrogen as unity, Scott found the vapour densities of the following substances to be—

Na	12.75 (11.5).	KI	92 (84).
K	19 (19.5).	RbCl	70 (60).
CsCl	89.5 (84.2).	CsI	133 (130).
FeCl ₃	68	AgCl	80 (71.7).

In brackets are given the densities corresponding with the formulæ, according to Avogadro-Gerhardt's law. This figure is not given for FeCl₃, because at the temperature

being 1). This shows that the molecule of potassium (like those of sodium, mercury, and zinc) contains but one atom. This is also the case with many other metals, judging by their melting-point depressions.¹⁹ The specific gravity of potassium at 15° is 0·87, and is therefore less than that of sodium, as is also the case with all its compounds.²⁰ Potassium decomposes water with great violence, evolving 45,000 heat units per atomic weight in grams. The heat evolved is sufficient to inflame the hydrogen, the flame being coloured violet from the presence of particles of potassium.²¹

With regard to the relation of potassium to hydrogen and oxygen, it is closely analogous to sodium in this respect. Thus, with hydrogen it forms potassium hydride, KH (between 200° and 411°), and with oxygen it gives a suboxide, K₄O, an oxide K₂O, and a peroxide, only more oxygen enters into the composition of the latter than in sodium peroxide; potassium peroxide has the composition KO₂, but it is probable that in the combustion of potassium an oxide KO is also formed. Metallic potassium, like sodium, combines with mercury.²² In a word,

at which it was determined a portion of the FeCl₃ was naturally decomposed, forming FeCl₂. If it was not decomposed, then a density 81 would correspond with the formula FeCl₃, and if the decomposition were 2FeCl₃ = 2FeCl₂ + Cl₂, then the density should be 54. With regard to the silver chloride, there is reason to think that the platinum decomposed this salt. The majority of Scott's results correspond so closely with the formulæ that a better agreement cannot be expected in such determinations. V. Meyer (1887) gives 93 as the density of KI.

¹⁹ The molecules of non-metals are more complex—for instance, H₂, O₂, O₃, Cl₂, &c. But arsenic, the superficial appearance of which recalls that of metals, but which in its chemical properties approaches more clearly to the non-metals, has a complex molecule containing As₄.

²⁰ As the atomic weight of potassium is greater than that of sodium, the volumes of the molecules, or the quotients of the molecular weight by the specific gravity, are greater for potassium compounds than for those of sodium, because both the denominator and numerator of the fraction increase. We cite for comparison the volumes of the corresponding compounds (see Chap. XV., note 24):

Na 24	NaHO 18	NaCl 28	NaNO ₃ 37	Na ₂ SO ₄ 54
K 45	KHO 27	KCl 39	KNO ₃ 48	K ₂ SO ₄ 66

²¹ The same precautions must be taken in decomposing water by potassium as have to be observed with sodium (Chap. II., note 8).

It must be observed that potassium decomposes carbonic anhydride and carbonic oxide when heated, the carbon being liberated and the oxygen taken up by the metal, whilst on the other hand charcoal takes up oxygen from potassium, as is seen from the preparation of potassium by heating potash with charcoal: hence the reaction, K₂O + C = K₂ + CO, is reversible and the relation is the same in this case as between hydrogen and zinc.

²² **Potassium forms alloys with sodium** in all proportions. The alloys containing 1 and 3 equivalents of potassium to 1 equivalent of sodium are *liquids*, like mercury at the ordinary temperature. Joannis, by determining the amount of heat developed by these alloys in decomposing water, found the evolution for Na₂K, NaK, NaK₂, and NaK₃ to be 44·5, 44·1, 43·8 and 44·4 thousand heat units respectively (for Na 42·6 and for K 45·4). The formation of the alloy NaK₂ is therefore accompanied by the development of heat,

the relation between sodium and potassium is as close as that between chlorine and bromine, or, better still, between fluorine and chlorine, as the atomic weight of sodium, 23, is as much greater than that of fluorine, 19, as that of potassium, 39, is greater than that of chlorine, 35.5.

The resemblance between **potassium** and **sodium** is so great that **their compounds** can only be easily **distinguished** in the form of certain of their salts. For instance, the acid potassium tartrate, $C_4H_5KO_6$ (cream of tartar), is distinguished by its sparing solubility in water and in alcohol, and in a solution of tartaric acid, whilst the corresponding sodium salt is easily soluble. Therefore, if a solution of tartaric acid is added in considerable excess to the solutions of the majority of potassium salts, a precipitate of the sparingly soluble acid salt is formed, which does not occur with salts of sodium. The chlorides KCl and NaCl easily give double salts K_2PtCl_6 and Na_2PtCl_6 , with platinic chloride, $PtCl_4$, and the solubilities of these salts are very different, especially in a mixture of alcohol and ether. The sodium salt is easily soluble, whilst the potassium salt is insoluble or almost so, and therefore the reaction with platinic chloride is that most often used for the separation of potassium from sodium, as is more fully described in works on analytical chemistry.

It is possible to distinguish these metals from each other and to detect the least traces of them, by means of their property of imparting different **colours** to a **flame**. The presence of a salt of sodium in a flame is recognised by a brilliant yellow coloration, whilst a pure potassium salt renders a colourless flame violet. However, in the presence of a sodium salt the pale violet coloration given by a potassium salt is quite indistinguishable, and it is at first sight impossible in this case to discover the potassium salt in the presence of that of sodium. But by decomposing the light given by a flame coloured by these metals or a mixture of them, by means of a prism, they are both easily distinguishable, because the yellow light emitted by the sodium salt depends on a group of light rays having a definite index of refraction which corresponds with the yellow portion of the solar spectrum, having the index of refraction of the Fraunhofer line (strictly speaking,

whilst the other alloys may be regarded as solutions of potassium or sodium in this alloy. The liquid alloy NaK_2 is now used for filling thermometers employed for temperatures above 360° , when mercury boils. Kurnakoff and Pushin (1901) re-determined the fusing-points of the alloys of Na with K, and came to the conclusion that only one definite compound, Na_3K_2 or Na_2K , is formed. It melts at 6.88° , and the point of fusion attains a minimum at -12.5° , when the proportion of the metals approaches that in NaK_2 . This point must be regarded as the eutectic or cryohydrate point (Chap. I., note 58) where those who follow the doctrine of phases do not recognise the formation of alloys of definite proportions. But this is still an undecided question.

group of lines) D, whilst the salts of potassium give a light from which these rays are entirely absent, but which contain rays of a red and violet colour. Therefore, if a potassium salt occur in a flame, on decomposing the light (after passing it through a narrow slit) by means of a prism, there will be seen red and violet bands of light situated at a considerable distance from each other; whilst if a sodium salt be present a yellow line will appear. If both metals occur simultaneously in

a flame and emit light, the spectrum lines corresponding to both the potassium and the sodium will appear simultaneously.

For convenience in carrying on this kind of testing, **spectroscopes** (fig. 82) are constructed,²³ consisting of a refracting prism and three tubes placed in the plane of the refracting angle of the prism. One of the tubes, C, has a vertical slit at the end, giving access to the light to be tested, which then passes into the tube (collimator) containing a lens, which

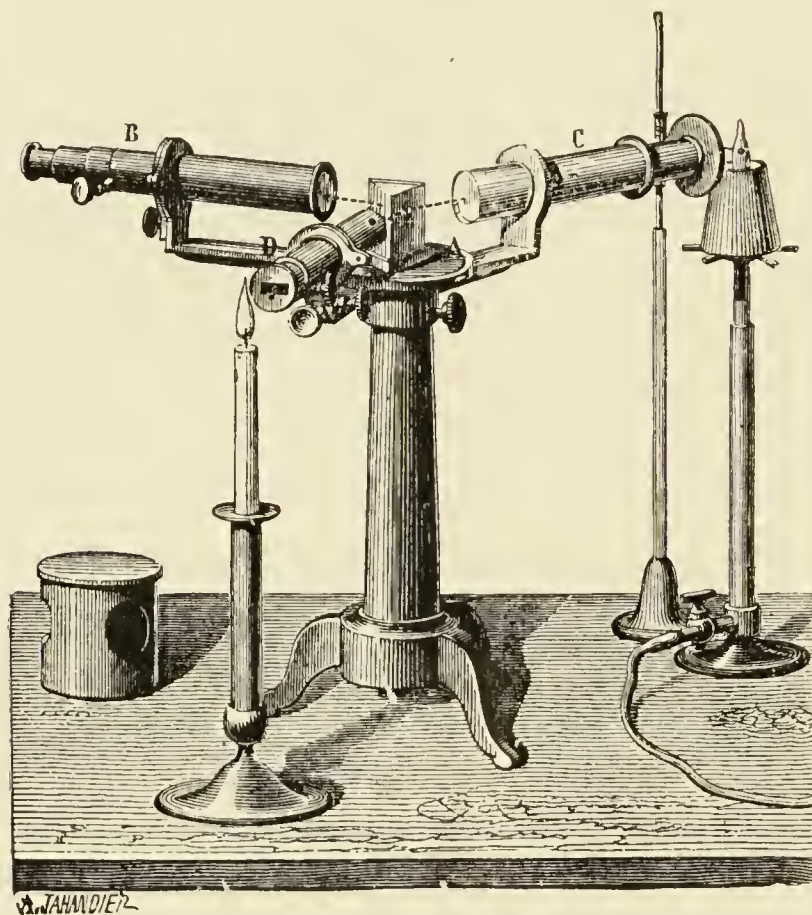


FIG. 82.—Spectroscope. The prism and table are covered with an opaque cover. The spectrum obtained from the flame coloured by a substance introduced on the wire is viewed through B. A light is placed before the scale D in order to illuminate the image of the scale reflected through B by the side of the prism.

gives the rays a parallel direction. The rays of light having passed through the slit, and having become parallel, are refracted and dispersed in the prism, and the spectrum formed is observed through the eyepiece of the other telescope B. The third tube D contains a horizontal

²³ For accurate measurements and comparative researches more complicated spectroscopes are required which give a greater dispersion, and are furnished for this purpose with several prisms—for example, in Browning's spectroscope the light passes through six prisms, and then, having undergone an internal total reflection, passes through the upper portion of the same six prisms, and again by an internal total reflection passes into the ocular tube. With such a powerful dispersion the relative positions of the spectral lines may be determined with accuracy. For the absolute and exact determination of the wave-lengths it is particularly important that the spectroscope should be furnished with diffraction gratings. The construction of spectroscopes destined for special purposes (for example, for investigating the light of stars, or for determining the absorption spectra in microscopic preparations, &c.) is exceedingly varied. Details of the subject must be looked for in works on physics and on spectrum analysis.

transparent scale (at the outer end) which is divided into equal divisions. The light from a source such as a gas burner or candle placed before this tube passes through the scale, and is reflected on that face of the prism which stands before the telescope B, so that the image of the scale is seen through this telescope simultaneously with the spectrum given by the rays passing through the slit of the tube C. In this manner the image of the scale and the spectrum given by the source of light under investigation are seen simultaneously. If the sun's rays be directed through the slit of the tube C, the observer looking through the eyepiece of B will then see the solar spectrum, and (if the aperture of the slit be narrow and the apparatus correctly adjusted) the dark Fraunhofer lines in it.²⁴ Small-sized spectrosopes are usually so adjusted that (looking through B) the violet portion of the spectrum is seen to the right and the red portion to the left, and the Fraunhofer line D (in the bright yellow portion of the spectrum) is situated on the 50th division of the scale.²⁵ If the light emitted by an incandescent solid—for example, the Drummond light—is passed through the spectroscope, then all the colours of the solar spectrum are seen, but not the dark Fraunhofer lines. To observe the result given by a flame coloured by various salts a Bunsen gas burner (or the pale flame of hydrogen gas issuing from a platinum orifice), giving so pale a flame that its spectrum will be practically invisible, is placed before the slit. If any compound of sodium be placed in the flame of the gas burner (for which purpose a platinum wire on whose end sodium chloride is fused is fixed to the stand), the flame will be coloured yellow, and on looking through the spectroscope the observer will see a bright **yellow** line falling upon the 50th division of the scale, which is seen together with the spectrum in the telescope. No yellow

²⁴ The arrangement of all the parts of the apparatus so as to give the clearest possible vision and accuracy of observation must evidently precede every kind of spectroscopic determination. Details concerning the practical use of the spectroscope must be looked for in special works on the subject. In this treatise the reader is supposed to have a certain knowledge of the physical data respecting the refraction of light, and its dispersion and diffraction, and the theory of light, which allows of the determination of the length of the waves of light in absolute measure on the basis of observations with diffraction gratings, the distance between whose divisions may be easily measured in fractions of a millimetre; by such means it is possible to determine the wave-length of any given ray of light.

²⁵ In order to give an idea of the size of the scale, we may observe that the ordinary spectrum extends from the zero of the scale (where the red portion is situated) to the 170th division (where the end of the visible violet portion of the spectrum is situated), and that the Fraunhofer line A (the extreme prominent line in the red) corresponds with the 17th division of the scale; the Fraunhofer line F (at the beginning of the blue, near the green colour) is situated on the 90th division, and the line G, which is clearly seen in the beginning of the violet portion of the spectrum, corresponds with the 127th division of the scale.

lines or other refractive index, nor any rays of any other colour, will be seen, and, therefore, the spectrum corresponding with sodium compounds consists of yellow rays of that index of refraction belonging to the Fraunhofer (black) line D of the solar spectrum. If a potassium salt be introduced into the flame instead of a sodium salt, two bands will predominate which are feebler than the bright sodium band—namely, one red line near the Fraunhofer line A and another violet line. Besides which, a pale, almost continuous, spectrum will be observed in the central portions of the scale. If a mixture of sodium and potassium salts be now introduced into the flame, three lines will be seen simultaneously—namely, the red and pale violet lines of potassium and the yellow line of sodium. In this manner it is possible, by the aid of the spectroscope, to determine the relation between the spectra of metals and known portions of the solar spectrum. The continuity of the latter is interrupted by dark lines (that is, by an absence of light rays of definite indices of refraction), termed the Fraunhofer lines of the solar spectrum. It has been shown by careful observations (by Fraunhofer, Brewster, Foucault, Ångström, Kirchhoff, Cornu, Lockyer, Dewar, and others) that there exists an exact **agreement between the spectra** of certain **metals** and certain of the **Fraunhofer** lines. Thus the bright yellow sodium line exactly corresponds with the distant dark Fraunhofer line D of the solar spectrum. A similar agreement is observed in the case of many other metals. This is not an approximate or a chance correlation. In fact, if a spectroscope having a large number of refracting prisms and a high magnifying power is used, it is seen that the bright line D of the sodium flame consists of an entire system of closely adjacent but definitely situated fine and wide (sharp, distinct) bright lines,²⁶ and an exactly similar group of dark lines is obtained when the solar spectrum is examined through the same apparatus, so that each bright sodium line exactly corresponds with a dark line in the solar spectrum.^{26a} This coincidence of the bright lines formed by sodium with the dark lines of the solar spectrum cannot be accidental. This conclusion is further confirmed by the fact that the bright lines of other metals correspond with dark lines of the solar spectrum. Thus, for example, a series of sparks passing between

²⁶ The two most distinct, D, or sodium lines, have wave-lengths of 0.0005890 and 0.0005896 of a millimetre, besides which fainter and fainter lines are seen whose wave-lengths in millionths of a millimetre are 588.7 and 588.1, 616.0 and 615.4, 515.5 and 515.2, 498.3 and 498.2, &c., according to Liveing and Dewar.

^{26a} In the ordinary spectroscopes which are usually employed in chemical research, one yellow band, which does not split up into thinner lines, is seen instead of the system of sodium lines, owing to the small dispersive power of the prism and the width of the slit of the object tube.

the iron electrodes of a Ruhmkorff coil gives 450 very distinct lines characterising this metal. All these 450 bright lines, constituting the whole spectrum corresponding with iron, are repeated, as Kirchhoff showed, in the solar spectrum as dark Fraunhofer lines which occur in exactly the same situations as the bright lines in the iron spectrum, just as the sodium lines correspond with the band D in the solar spectrum. Many observers have in this manner studied the solar spectrum and the spectra of different metals simultaneously, and have discovered, in the former, lines which correspond not only with sodium and iron, but also with many other metals.²⁷ The spectra of such

²⁷ The most accurate measurements (observations) made in this respect are carried out with diffraction gratings, because in this case the positions of the dark and bright lines do not depend on the index of refraction of the material of the prism. The best—that is, the most general and accurate—method of expressing the results of such determinations consists in determining the lengths of the waves corresponding to the rays of a definite index of refraction. (Sometimes instead of this the fraction of 1 divided by the square of the wave-length is given.) We shall express this *wave-length* in *millionth parts of a millimetre* (the ten-millionth parts are often doubtful, and fall within the limits of error). In order to illustrate the relation between the wave-lengths and the positions of the lines of the spectrum, we will cite the wave-lengths corresponding with the chief Fraunhofer lines and colours of the spectrum.

Fraunhofer line	A	B	C	D	E	b	F	G	H
Wave-length	760·8	687·0	656·3	589·6—589·0	527·0	518·4—516·8	486·1	430·8	396·9
Colour	red			orange		yellow	green	blue	violet

It may be mentioned that the *red* colour corresponds with lines having a wave-length of from 780 (with a greater wave-length the lines are hardly visible, and are ultra-red) to 650, the *orange* from 650 to 590, the *yellow* from 590 to 520, the *green* from 520 to 490, the *blue* from 490 to 420, and the *violet* from 420 to 380 millionth parts of a millimetre. Beyond 380 the lines are scarcely visible, and belong to the ultra-violet. The lines C and F are peculiar to hydrogen, D to sodium, E, G, and H to iron and calcium, A and B to oxygen.

In the following table are given the *wave-lengths* of the light spectra (the longest and most distinct, see later) for certain elements, which are obtained either in the flame of a Bunsen's burner or in Geissler tubes, or by an electric discharge. In the table the figures in black type correspond with lines which are so bright and distinctly visible that they may be made use of, both in determining the relation between the divisions of the scale and the wave-lengths, and in determining the admixture of a given element with another. A dash separates those lines between which several other lines are clearly visible if the dispersive power of the spectroscope is sufficiently high to render visible the neighbouring lines. Neither the ultra-red (wave-length greater than 790) nor the ultra-violet (wave-length less than 320; these are active in photography) spectral lines, which have been discovered in the spectra of many elements, are given in this table, because they are not directly visible in the spectroscope. The wave-lengths are given in millionth parts of a millimetre. The *length* of the lines does not always correspond with their brilliancy. According to Lockyer this length is determined by placing the carbon electrodes (between which the incandescent vapours of the metals are formed), not horizontally to the slit (as they are generally placed, to give more light), but vertically to it. Then certain lines appear long and others short. As a rule (Lockyer, Dewar, Cornu), the longest lines are those with which it is easiest to obtain *reversed* spectra (see later). Consequently these lines are the most characteristic. Only the longest and most brilliant are given in our

taining rarefied gases, through which the discharge of a Ruhmkorff coil is passed. Thus hydrogen gives a spectrum composed of a bright-red line corresponding with the Fraunhofer line C (wave-length 656·3), a bright bluish-green line corresponding with the line F (486·1), and two faint violet lines with wave-lengths G 410·1 and 434·0 thousandths of a micron. Of these rays the red is the brightest, and therefore the general colour of luminous hydrogen (with an electric discharge through a Geissler tube) is reddish.

The correlation of the Fraunhofer lines with the spectra of metals depends on the phenomenon of the so-called **reversal of the spectrum**. This phenomenon consists in this, that instead of the bright spectrum corresponding with a metal, under certain circumstances a similar dark spectrum in the form of Fraunhofer lines may be obtained, as will be explained directly. In order to clearly understand the phenomenon of reversed spectra it must be known that when light passes through certain transparent substances these substances retain rays of a certain refrangibility. The colour of solutions is a proof of this. Light which has passed through a yellow solution of a uranium salt contains no violet rays, and after having passed through a red solution of a permanganate, light contains but few rays in the yellow, blue, and green portions of the spectrum. Solutions of copper salts absorb nearly all red rays. Sometimes colourless solutions also absorb rays of certain definite refractive indices and give **absorption spectra**. Thus solutions of salts of didymium absorb rays of a certain refrangibility, and therefore an impression of black lines is received,²³ as shown in

²³ The method of observing absorption spectra consists in taking a continuous spectrum of white light (one which does show either dark lines or particularly bright luminous bands—for instance, the light from a candle, lamp, or other source). The collimator (that is, the tube with the slit) is directed towards this light, and then all the colours of the spectrum are visible in the ocular tube. A transparent absorptive medium—for instance, a solution or a tube containing a gas—is then placed between the source of light and the apparatus (or anywhere inside the apparatus itself in the path of the rays). In this case either the entire spectrum is uniformly fainter, or absorption bands appear on the bright field of the continuous spectrum in definite positions along it. These bands have different lengths and positions, and distinctness and intensity of absorption, according to the properties of the absorptive medium. Like the luminous spectra given by incandescent gases and vapours, the absorption spectra of a number of substances have already been studied, and some with great precision—as, for example, the spectrum of the brown vapours of nitrogen dioxide by Hasselberg (at Pulkowa); the spectrum of a long column of oxygen under pressure (N. G. Egoroff and others); the spectra of colouring matters (Eder and others), especially of those applied to orthochromatic photography; the spectra of blood, chlorophyll (the green constituent of leaves), and other similar substances—all the more carefully, as by the aid of their spectra the presence of these substances may be also discovered in small quantities (even in microscopical quantities by the aid of special appliances on the microscope) and the changes they undergo investigated.

fig. 83. Many vapours (iodine) and gases (nitric peroxide) give similar spectra. Light which has passed through a deep layer of aqueous vapour, oxygen, or nitrogen also gives an absorption spectrum. For this reason the peculiar (winter) dark lines discovered by Brewster are observed in sunlight, especially in the evening and morning, when the sun's rays pass through the atmosphere (containing these substances)

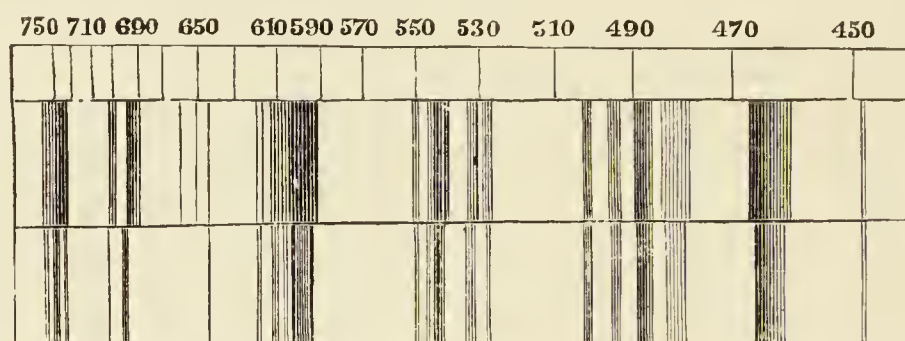


FIG. 83.—Absorption spectrum (Lecoq de Boisbaudran) of salts of didymium in concentrated and dilute solutions.

by a longer path than at midday. It is evident that the Fraunhofer lines may be ascribed to the absorption of certain rays of light in its passage from the luminous mass of the sun to the earth. The remarkable progress made in all spectroscopic research dates from the **investigations** made by **Kirchhoff** (1859) on the relation between absorption spectra and the spectra of luminous incandescent gases. It had already been observed long before (by Fraunhofer, Foucault, Ångström) that the bright spectrum of the sodium flame gives two bright lines which are in exactly the same position as two black lines known as D in the solar spectrum, which evidently belong to an absorption spectrum.

The absorption spectra, obtained at the ordinary temperature and proper to substances in all physical states, offer a most extensive but as yet little studied field, both for the general theory of spectroscopy and for gaining an insight into the structure of



FIG. 84.—Absorption spectra of nitrogen dioxide and iodine.

substances. The investigation of colouring matters has already shown that in certain cases a definite change of composition and structure entails not only a definite change of the colours, but also a displacement of the absorption bands by a definite number of wave-lengths.

When Kirchhoff caused diffused sunlight to fall upon the slit of a spectroscope, and placed a sodium flame before it, a perfect superposition was observed—the bright sodium lines completely covered the black lines D of the solar spectrum. When, further, the continuous spectrum of a Drummond light showed the black line D on placing a sodium flame between it and the slit of the spectroscope—that is, when the Fraunhofer line of the solar spectrum was artificially produced—there was no doubt that its appearance in the solar spectrum was due to the light passing somewhere through incandescent vapours of sodium. Hence a new theory of **reversed spectra**²⁹—that is, of the relation between the waves of light emitted and absorbed by a substance under given conditions of temperature—arose, and this is expressed by Kirchhoff's law, discovered by a careful analysis of the phenomena. This law may be formulated in an elementary way as follows: At a given temperature the relation between the intensity of the light emitted (of a definite wave-length) and the absorptive capacity with respect to the same colour (of the same wave-length) is a constant quantity.³⁰ As a black dull surface emits and also absorbs a considerable quantity of heat rays whilst a polished metallic surface both absorbs and emits but few, so a flame coloured by sodium emits a considerable quantity of yellow rays of a definite refrangibility, and has the property of absorbing a considerable quantity of the rays of the same refractive index. In general the medium which emits definite rays also absorbs them.

Thus the bright spectral rays characteristic of a given metal may

²⁹ A number of methods have been invented to demonstrate the reversibility of spectra; of these methods we shall cite two which are very easily carried out. In Bunsen's method sodium chloride is put into an apparatus for evolving hydrogen (the spray of the salt is then carried off by the hydrogen and colours the flame with the yellow sodium colour), and the hydrogen is ignited in two burners—one a large one, with a wide flame giving a bright yellow sodium light, and the other with a small fine orifice and giving a pale flame: this latter flame will throw a dark patch on the large bright flame. In Sadoffsky's method the front tube, C (p. 578), is unscrewed from a spectroscope directed towards the light of a lamp (a continuous spectrum), and the flame of a spirit lamp coloured by a small quantity of NaCl is placed between the tube and the prism; a black band corresponding to sodium will then be seen on looking through the ocular tube. This experiment is always successful if the requisite relation between the intensities of the lights of the two lamps is maintained.

³⁰ The absorptive capacity is the relation between the intensities of the light (of a given wave-length) falling upon and of that retained by a substance. Bunsen and Roscoe showed by direct experiment that this ratio is a constant quantity for every substance. If A stand for this ratio for a given substance at a given temperature—for instance, for a flame coloured by sodium—and E be the intensity of the light of the same wave-length emitted at the same temperature by the same substance, then Kirchhoff's law, the explanation and deduction of which must be looked for in text-books of physics, states that the fraction A/E is a constant quantity depending on the nature of a substance (as A depends on it) and on the temperature and wave-length.

be reversed—that is, converted into dark lines—by passing light which gives a continuous spectrum through a space containing the heated vapours of the metal. A similar phenomenon to that thus artificially produced must be also recognised as taking place in sunlight, which shows dark lines characteristic of known metals—that is, the Fraunhofer lines form an absorption spectrum or depend on a reversed spectrum, it being presupposed that the sun itself, like all known sources of artificial light, gives a continuous spectrum without Fraunhofer lines.³¹ We must imagine that the sun, owing to its high temperature, emits a brilliant light which gives a continuous spectrum, and that this light, before reaching our eyes, passes through a space full of the vapours of different metals and their compounds. As the earth's atmosphere³² contains very little, or no, metallic vapours, and as they cannot be supposed to exist in celestial space,^{32a} the only place in which the existence of such vapours can be admitted is in the **atmosphere surrounding the sun itself**. As the cause of the sun's luminosity must be looked for in its high temperature, the existence of an atmosphere containing metallic vapours is readily understood, because at that high temperature such metals as sodium, and even iron (under the comparatively low pressure prevalent on the surface of the sun), are separated from their compounds and converted into vapour. Thus the sun must be imagined as surrounded by an atmosphere of incandescent

³¹ Heated metals begin to emit light (only visible in the dark) at about 420° (varying with the metal). On further heating, solids first emit red, then yellow, and lastly white light. Compressed or heavy gases (see Chap. III., note 44), when strongly heated, also emit white light. Heated liquids (for example, molten steel or platinum) also give a white compound light. This is readily understood. In a dense mass of matter the collisions of the molecules and atoms are so frequent that waves of only a few definite lengths cannot appear; the reverse is possible in rarefied gases or vapours.

³² Brewster, as is mentioned above, first distinguished the atmospheric, cosmical Fraunhofer lines from the solar lines. Janssen showed that the spectrum of the atmosphere contains lines which depend on the absorption produced by aqueous vapour. Egoroff, Olszewski, Janssen, and Liveing and Dewar showed by a series of experiments that the oxygen of the atmosphere gives rise to certain lines of the solar spectrum, especially the line A. Liveing and Dewar took a layer of 165 cm. of oxygen compressed under a pressure of 85 atmospheres, and determined its absorption spectrum, and found that, besides the Fraunhofer lines A and B, it contained the following groups: 630–622, 581–568, 535, 480–475. The same lines were found for liquid oxygen. But oxygen in the Geissler tube does not give these lines and bands, because the temperature and density are different.

^{32a} If the material of the whole heavenly space formed the absorbent medium, the spectra of the stars would be the same as the solar spectrum; but Huyghens, Lockyer, and others showed not only that this is the case for only a few stars, but that the majority of stars give spectra of a different character with dark and bright lines and bands, which differ in different kinds of stars. This subject belongs to the province of astro-physics.

vaporous and gaseous matter,³³ including those elements whose reversed spectra correspond with the Fraunhofer lines—namely, sodium, iron, hydrogen, lithium, calcium, magnesium, &c. Thus in spectrum analysis we find a means of determining the composition of the inaccessible heavenly luminaries, and much has been done in this respect since Kirchhoff's theory was formulated. By observations on the spectra of many heavenly bodies, changes have been discovered going on in them,³⁴ and many of the elements known to us have been detected with certainty in them.³⁵ From this it must be concluded that the same

³³ Eruptions, in some respects like our volcanic eruptions, but on an incomparably larger scale, and proceeding in the dense vaporous mass of the sun's nucleus, are of frequent occurrence on the sun. They are seen as protuberances, visible during a total eclipse of the sun, in the form of vaporous masses on the edge of the solar disc and emitting a faint light. These protuberances of the sun are now observed at all times by means of the spectroscope (Lockyer and Janssen's method) because they contain luminous vapours (giving bright lines) of hydrogen and other elements.

³⁴ The great interest and vastness of astro-physical observations concerning the sun, comets, stars, nebulae, &c., render this new province of natural science very important, and necessitate referring the reader to special works on the subject.

The most important astro-physical data since the time of Kellner are those referring to the *displacement* of the lines of the spectrum. Just as a musical note changes its pitch with the approach or withdrawal of the resonant object or the ear, so the pitch of the luminous note or wave-length of the light varies if the luminous (or absorbent) vapour and the earth from which we observe it, approach or recede from each other; this expresses itself in a visible displacement of the spectral lines. The solar eruptions even give broken lines in the spectrum, because the rapidly moving eruptive masses of vapour and gases either travel in the direction of the eye or fall back towards the sun. As the earth travels with the solar system among the stars, so it is possible to determine the direction and velocity with which the sun travels in space by the displacement of the spectral lines and light of the stars. The changes proceeding on the sun, both in its mass, which must be regarded as vaporous, and in its atmosphere, are now studied by means of the spectroscope. For this purpose, many special astro-physical observatories now exist where these investigations are carried on.

We may remark that if the observer or luminous object moves with a velocity $\pm v$, the ray, whose wave-length is λ , has an apparent wave-length $\lambda \frac{n \pm v}{n}$, where n is the velocity of light. Thus Tolon, Huyghens and others proved that the star Aldebaran approaches the solar system with a velocity of 30 kilometres per second, while Arcturus is receding with a velocity of 45 kilometres.

³⁵ Spectrum analysis has proved the indubitable existence in the sun and stars of a number of elements known in chemistry. Huyghens, Secchi, Lockyer, and others have furnished a large amount of material upon this subject. A compilation of existing information on it has been given by Prof. I. A. Kleiber, in the Journal of the Russian Physico-chemical Society for 1885 (vol. xviii. p. 146). The peculiar element called **helium** first discovered by means of spectroscopy, is characterised by a line (whose wave-length is 587.5, situated near D), which is seen very brightly in the projections (protuberances) and spots of the sun; it was subsequently found on the earth (Chap. IX.). Great caution is however necessary in drawing any definite conclusions from the spectra of the elements, because they vary in the brilliancy and position of their lines with changes of temperature and pressure. Thus, for instance, Lockyer could only see the line 423, at the very end of the calcium spectrum, at comparatively low temperatures, whilst the lines 397 and 393 appear at a higher temperature, and at a still higher temperature the line 423 becomes quite invisible.

elements which exist on the earth occur throughout the whole universe, and that even at that degree of temperature maintained on the sun those simple substances which we accept as the elements in chemistry remain unchanged. A high temperature forms one of those conditions under which compounds most easily decompose; and if sodium or a similar element were a compound, in all probability it would be decomposed into its component parts at the high temperature of the sun, and this would have a corresponding effect on its spectrum. This may indeed be concluded from the fact that in ordinary spectroscopic experiments the spectra obtained often belong to the metals and not to the compounds taken; this depends on the decomposition of these compounds in the heat of the flame. If common salt is introduced into the flame of a gas-burner, a portion of it is decomposed, first reacting, in all probability, with water, and forming hydrochloric acid and sodium hydroxide, the latter then becoming partially decomposed by the hydrocarbons, giving metallic sodium, the incandescent vapour of which emits light of a definite refrangibility. This conclusion is arrived at from the following experiment:—If hydrochloric acid gas is introduced into a flame coloured by sodium, it is observed that the sodium spectrum disappears, owing to the fact that metallic sodium cannot remain in the flame in the presence of an excess of hydrochloric acid. The same thing takes place on the addition of sal-ammoniac, which in the heat of the flame gives hydrochloric acid. If a porcelain tube containing sodium chloride (or sodium hydroxide or carbonate), and closed at both ends by glass plates, is so powerfully heated that the salt volatilises, the sodium spectrum is not observable; but if the salt be replaced by sodium, then either the bright line or the absorption spectra will be obtained, according to whether light emitted by the incandescent vapour be observed, or light passing through the tube. Thus the above spectrum is not given by sodium chloride or other sodium compound, but is proper to the metal sodium itself. This is also the case with other analogous metals. The chlorides and other halogen **compounds** of barium, calcium, copper, &c., give independent spectra which differ from those of the metals. If barium chloride be introduced into a flame, it gives a mixed spectrum belonging to metallic barium and barium chloride. If, besides barium chloride, hydrochloric acid or sal-ammoniac be introduced into the flame, then the spectrum of the metal disappears, and there remains that of the chloride, which differs distinctly from the spectrum of barium fluoride, barium bromide, or barium iodide. A certain common resemblance and certain common lines are observed in the spectra of two different compounds of one and the same element obtained in the above-described manner, and also in

the spectrum of the metal, but they all have their peculiarities. The independent spectra of the compounds of copper are easily observed (fig. 85). Thus certain compounds which exist in a state of vapour, and

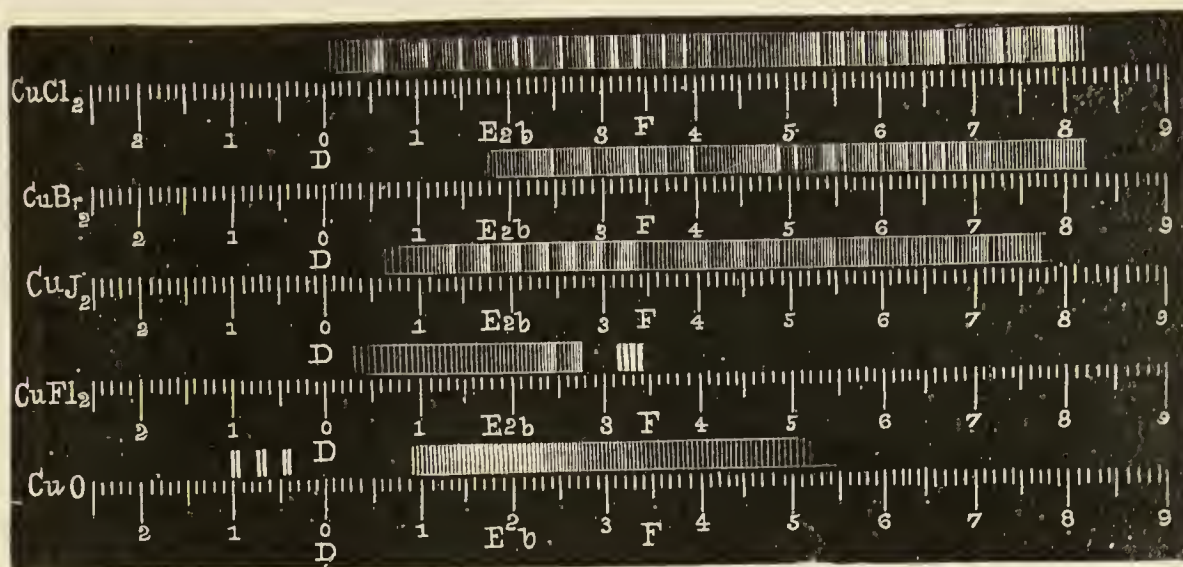


FIG. 85—Bright spectra of copper compounds.

are luminous at a high temperature, give their independent spectra. In the majority of cases the spectra of compounds are composed of indistinct luminous lines and complete bright bands, whilst metallic elements generally give a few clearly defined spectral lines.³⁶ There is

³⁶ Spectroscopic observations are still further complicated by the fact that one and the same substance gives different spectra at different temperatures. This is especially the case with gases the spectra of which are obtained by an electric discharge in tubes. Plücker, Wüllner, Schuster, and others showed that at low temperatures and pressures the spectra of iodine, sulphur, nitrogen, oxygen, &c., are quite different from those of the same elements at high temperatures and pressures. This may either depend on the fact that the elements change their molecular structure with a change of temperature just as ozone is converted into oxygen (for instance, from N_2 molecules are obtained containing only one atom of nitrogen), or else it may be because at low temperatures certain rays have a greater relative intensity than those which appear at higher temperatures. If we suppose that the molecules of a gas are in continual motion, with a velocity dependent on the temperature, then it must be admitted that they often strike against each other and rebound, and thus communicate peculiar motions to each other and the supposed ether, which express themselves in luminous phenomena. A rise of the temperature or an increase in the density of a gas must have an influence on the collision of its molecules and on the luminiferous vibrations thus produced, and this may be the cause of the difference of the spectra under these circumstances. It has been shown by direct experiment that gases compressed by pressure, when the collision of the molecules must be frequent and varied, exhibit on the passage of an electric spark a more complex spectrum than rarefied gases, and that even a continuous spectrum appears. In order to show the variability of the spectrum according to the circumstances under which it proceeds, it may be mentioned that potassium sulphate fused on a platinum wire gives, on the

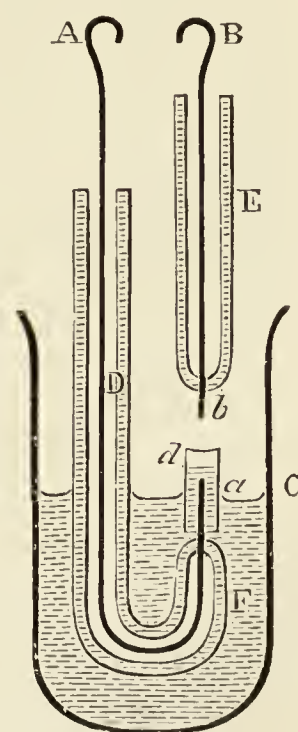


FIG. 86.—Method of showing the spectrum of substances in solution.

no reason for supposing that the spectrum of a compound is equal to the sum of the spectra of its elements—that is, in all probability, **every compound** which is not decomposed by heat **has its own proper spectrum**. This is best proved by absorption spectra, which are essentially only reversed spectra observed at low temperatures. If every salt of sodium, lithium, and potassium gives one and the same spectrum, this must be ascribed to the presence in the flame of the free metals liberated by the decomposition of their salts. Therefore the phenomena of the spectrum are determined by molecules, and not by the atoms they contain—that is, the molecules of the metal sodium, and not its atoms, produce those particular vibrations which determine the spectrum of a sodium salt. Where there are no free molecules of metallic sodium there is no sodium spectrum, although its atoms may be present.^{36a}

Spectrum analysis has not only endowed science with a knowledge of the composition of distant heavenly bodies (of the sun, stars, nebulae, comets, &c.), but has also given a new **method** for studying the matter of the earth's surface. With its help Bunsen discovered

passage of a series of sparks, a distinct system of lines, 583–578, whilst when a series of sparks is passed through a solution of this salt this system of lines is faint, and when Roscoe and Schuster observed the absorption spectrum of the vapour of metallic potassium (which is green) they remarked a number of lines of the same intensity as the above system in the red, orange, and yellow portions.

The spectra of solutions are best observed by means of Lecoq de Boisbaudran's arrangement, shown in fig. 86. A bent capillary tube, D F, inside which a platinum wire *a* (from 0.3 to 0.5 mm. in diameter) is fused, is immersed in a narrow cylinder, C (in which it is firmly held by a cork). The projecting end, *a*, of the wire is covered by a fine capillary tube, *d*, which extends 1–2 mm. beyond the wire. Another straight capillary tube, E, with a platinum wire, B*b*, about 1 mm. in diameter (a finer wire soon becomes hot), is held (by a cork or in a stand) above the end of the tube, D. If the wire A is now connected with the positive, and the wire B with the negative terminal of a Ruhmkorff's coil (if the wires are connected in the opposite order, the spectrum of air is obtained), a series of sparks rapidly following each other appear between *a* and *b*, and their light may be examined by placing the apparatus in front of the slit of a spectroscope. The variations to which a spectrum is liable may easily be observed by increasing the distance between the wires, altering the direction of the current or strength of the solution, &c.

^{36a} The relation between spectroscopic phenomena and the composition of bodies is complicated by two chief factors: in the first place by the high temperature (in the flame or electric arc), at which we cannot always be sure of the changes taking place in the distribution of the atoms; in the second place experiment clearly shows that the spectra of gases and vapours vary greatly (some lines disappear, others appear, and the brilliancy or intensity and width of separate lines undergoes great change) according to the temperature, relative (partial) pressure or density, action of a magnetic field, &c. (for instance, in Geissler tubes with nitrogen, oxygen, &c., different spectra are observed at the cathode and anode). However, the spectroscope gives an insight into much, both in the distant and vast worlds of the stars, and in the infinitely minute universe of molecules, and the further development of this subject promises to enlighten much in respect to atoms and molecules.

two new elements belonging to the group of the alkali metals, and thallium, indium, and gallium were afterwards discovered by the same means. The spectroscope is employed in the study of rare metals (which in solution often give distinct absorption spectra), of dyes, and of many organic substances, &c.³⁷ With respect to the metals which are analogous to sodium, they all give similar very volatile salts and such very characteristic spectra that the least traces of them³⁸ are discovered with great ease by means of the spectroscope.

³⁷ The importance of the spectroscope for the purpose of chemical research was already shown by Gladstone in 1856, but it did not become an accessory to the laboratory until after the discoveries of Kirchhoff and Bunsen. It may be hoped that in time spectroscopic researches will meet certain wants of the theoretical (philosophical) side of chemistry, but as yet all that has been done in this respect can only be regarded as attempts which have not yet led to any trustworthy conclusions. Thus many investigators, by collating the wave-lengths of all the light vibrations excited by a given element, endeavour to find the law governing their mutual relations; others (especially Hartley and Ciamician), by comparing the spectra of analogous elements (for instance, chlorine, bromine, and iodine), have succeeded in noticing definite features of resemblance in them, whilst others (Grünwald) search for relations between the spectra of compounds and their component elements, &c.; but owing to the multiplicity of the spectral lines proper to many elements, and (especially in the ultra-red and ultra-violet ends of the spectrum) the existence of lines which are indistinguishable owing to their faintness, and also owing to the comparative novelty of spectroscopic research, this subject cannot be considered as in any way perfected. Nevertheless in certain instances there is evidently some relationship between the wave-lengths of all the spectral lines formed by a given element. Thus, in the hydrogen spectrum the wave-length $= 364.542 m^2/(m^2 - 4)$, if m varies as a series of whole numbers from 3 to 15 (Walmer, Hagebach, and others). For example, when $m=3$, the wave-length of one of the brightest lines of the hydrogen spectrum is obtained (656.2); when $m=7$, one of the visible violet lines (396.8), and when m is greater than 9, the ultra-violet lines of the hydrogen spectrum. Such similar elements as K, Rb and Cs or Ca, Sr, and Ba exhibit (L. de Boisbaudran, Rydberg, Hartley, Kayser and Runge, &c.) a distinct parallelism in their spectra in the fact that corresponding lines or groups of lines (double or triple lines, &c.) move in a definite direction as the atomic weight increases. H. Ramage (Cambridge, 1902) showed this with peculiar clearness by taking into consideration not only the relative brilliancy of the lines, but also their capacity to give the Zeeman effect (widening of the lines in a magnetic field). For instance the blue ends of the spectra of K, Rb, and Cs exhibit brilliant analogous double lines with wave-lengths:—

K	Rb	Cs
404.7 and 404.4	421.6 and 420.2	459.3 and 455.8

In the oxy-hydrogen flame Ca, Sr, and Ba give one particularly distinct (brilliant) line, having a wave-length of 422.7 for Ca, 460.8 for Sr, and 553.6 for Ba. In either case the variation proceeds in the direction of the red end of the spectra with a rise in the atomic weight. All such instances show the germ of a connection between the atomic weights, chemical analogies, and the position of the spectral lines of the elements. But I do not think we yet grasp the exact laws which govern this relation, but see only a reflection of the periodic law (Chap. XV.).

³⁸ In order to show the degree of sensitiveness of spectroscopic reactions the following observations of Dr. Bence Jones may be cited: If a solution of 3 grains of a lithium salt be injected under the skin of a guinea-pig, after the lapse of four minutes, lithium can be discovered in the bile and liquids of the eye, and, after ten minutes, in all parts of the animal.

For instance, *lithium* gives a very *brilliant red* coloration to a flame and a very bright red spectral line (wave-length, 670·8 millionths mm.), with a bright orange (610·4) line beside it, which indicates the presence of this metal in admixture with compounds of other alkali metals.

Lithium, Li, is, like potassium and sodium, somewhat widely spread in silicious rocks, but only occurs in small quantities and as mere traces in considerable masses of potassium and sodium salts. Only a very few rather rare minerals contain more than traces of it³⁹—for example, spodumene and lithia mica, although many compounds of lithium are in all respects closely analogous to the corresponding compounds of sodium and potassium; the *carbonate* is sparingly soluble in cold water, which fact is taken advantage of for separating lithium from potassium and sodium. This salt, Li_2CO_3 , is easily converted into the other compounds of lithium. Thus, for instance, the hydroxide, LiHO , is obtained in exactly the same way as caustic soda, by the action of lime on the carbonate, and it is soluble in water and crystallises (from its solution in alcohol) as $\text{LiHO}, \text{H}_2\text{O}$. Metallic *lithium* is obtained by the action of a galvanic current on fused lithium chloride; for this purpose a cast-iron crucible, furnished

³⁹ Thus *spodumene* contains up to 6 per cent., and *petalite*, and *lepidolite* or lithia mica, about 3 per cent. of lithium oxide. This mica is met with in certain granites in a somewhat considerable quantity, and is therefore most frequently employed for the preparation of lithium compounds. The treatment of lepidolite is carried on on a large scale, because various salts of lithium are employed in medicine as a remedy for certain diseases (stone, gouty affections), as they have the power of dissolving the insoluble uric acid which is then deposited. Lepidolite, which is unacted on by acids in its natural state, decomposes under the action of strong hydrochloric acid after it has been fused. After being subjected to the action of the hydrochloric acid for several hours all the silica is obtained in an insoluble form, whilst the metallic oxides pass into solution as chlorides. The solution is mixed with nitric acid to convert the ferrous salts into ferric, and sodium carbonate is then added until the liquid becomes neutral, by which means a precipitate is formed of the oxides of iron, alumina, magnesia, &c., as insoluble oxides and carbonates. The solution then contains the chlorides of the alkaline metals, KCl , NaCl , and LiCl , which do not give a precipitate with sodium carbonate in a dilute solution. It is then evaporated, and a strong solution of sodium carbonate added. This precipitates lithium carbonate, which, although soluble in water, is much less so than sodium carbonate, and therefore the latter precipitates lithium from strong solutions as carbonate. *Lithium carbonate* is very slightly soluble in water. In this respect lithium forms a transition between the metals of the alkalies to magnesium, calcium, &c., the carbonates of which are only sparingly soluble. Oxide of lithium, Li_2O , may be obtained by heating the carbonate with charcoal. Lithium oxide in dissolving gives (per gram-molecule) 26,000 heat units; but the combination of Li_2 with O evolves 140,000 calories—that is, more than Na_2O (100,000 calories) and K_2O (97,000 calories), as shown by Beketoff (1887).

LiCl , LiBr , and LiI are soluble and form crystallo-hydrates with H_2O , $2\text{H}_2\text{O}$, and $3\text{H}_2\text{O}$, and recall the properties of Ca rather than those of Na. LiF is but slightly soluble (in 800 parts) in water (and still less so in a solution of NH_4F). The phosphate Li_3PO_4 is also but slightly soluble, and this may be taken advantage of for separating the metal from Na and K.

with a stout cover, is filled with lithium chloride, heated until the latter fuses, and a strong galvanic current then passed through the molten mass. The anode (where chlorine is evolved) (fig. 87) consists of a dense carbon rod, C (surrounded by a porcelain tube, P, fixed in an iron tube, BB), and the cathode of an iron wire, on which the metal is deposited. When a somewhat considerable quantity of the metal has accumulated on the wire it is withdrawn, the metal collected from it, and the experiment then carried on as before.^{39a} Lithium is the lightest of all metals, its specific gravity being 0.59, so that it floats even on naphtha; it melts at about 185°, but does not volatilise at a red heat. Its appearance recalls that of sodium, and, like it, it has a yellow tint. At 200° it burns in air with a very bright flame, forming lithium oxide. When heated, lithium easily and rapidly combines with nitrogen, forming nitride of lithium, Li_3N (Ouvrard, 1892, Guntz), which forms ammonia with water and combines with hydrogen, forming lithium hydride, LiH ($\text{NLi}_3 + 3\text{H}_2 = \text{NH}_3 + 3\text{LiH}$), which again forms the nitride and ammonia when acted on by nitrogen. In decomposing water it does not ignite the hydrogen. The characteristic test for lithium compounds is the **red coloration** which they impart to a colourless flame.⁴⁰

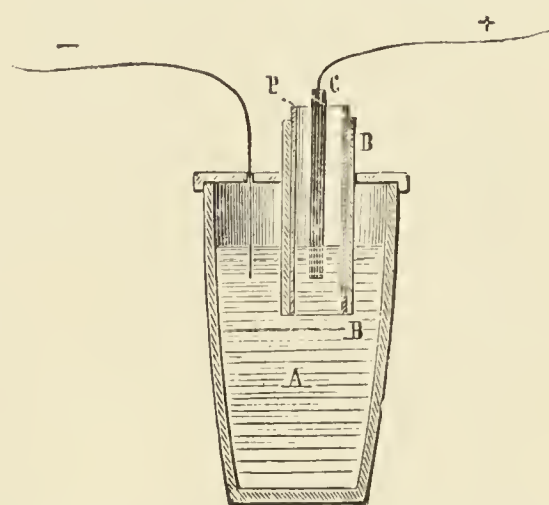


FIG. 87.—Preparation of lithium by the action of a galvanic current on fused lithium chloride.

Bunsen in 1860 tried to determine by means of the spectroscope whether any other as yet unknown metals might not occur in different natural products together with lithium, potassium, and sodium, and he soon discovered two new alkali metals showing independent spectra. They are named after the colour of their spectral lines and after the characteristic coloration which they impart to the flame. One which gives a red and a violet band is named **rubidium**, from *rubidius* (dark red), and the other **cæsium**, because it colours a pale flame sky-blue, which depends on its containing bright blue rays, appearing in the

^{39a} Guntz (1893) recommends adding KCl to the LiCl in preparing Li by this method, and the use of a current of 10 ampères at 20 volts, and a temperature not above 450°, so as to avoid the formation of Li_2Cl .

⁴⁰ In determining the presence of lithium in its compounds it is best to treat the material under investigation with acid (in the case of mineral silicon compounds, hydrofluoric acid must be taken), and to treat the residue with sulphuric acid, evaporate to dryness, and extract with alcohol, which dissolves a certain amount of the lithium sulphate. It is easy to discover lithium in such an alcoholic solution by means of the coloration imparted to the flame on burning it, and by investigating its light in a spectroscope. Lithium was first discovered in 1817 in petalite by Arfvedson.

spectrum of caesium as two blue bands (pp. 459 and 455). Both metals accompany sodium, potassium, and lithium, but in small quantities; rubidium occurs in larger quantity than caesium. The amount of the oxides of caesium and rubidium in lepidolite does not generally exceed one-half per cent. Rubidium has also been found in the ashes of many plants, while the Stassfurt carnallite (the mother liquor obtained after having been treated for KCl) forms a source (0.025 per cent.) for rubidium and also partly for caesium. Rubidium also occurs, although in very small quantities, in the majority of mineral waters. In a very few cases caesium is not accompanied by rubidium; thus, in a certain granite on the isle of Elba, caesium has been discovered, but not rubidium. This granite includes a very rare mineral called *pollux* which contains as much as 34 per cent. of caesium oxide. Guided by the spectroscope, and aided by the fact that the double salts of platinic chloride with rubidium and caesium chlorides are still less soluble in water than the corresponding potassium salt, K_2PtCl_6 ,⁴¹ Bunsen succeeded in separating the two metals from each other and from potassium, and demonstrated the great resemblance they bear to each other. The free metals,⁴² rubidium and caesium, which easily distil and are inflammable, have respectively the specific gravities 1.52 and 2.366, and the melting-points 39° and 27° , as was shown by N. N. Beketoff (1894),

⁴¹ The salts of the majority of metals are precipitated as carbonates on the addition of ammonium carbonate—for instance, the salts of calcium, iron, &c. The alkalis, whose carbonates are soluble, are not, however, precipitated in this case. On evaporating the resultant solution and igniting the residue (to remove the ammonium salts), we obtain salts of the alkali metals. They may be separated by adding hydrochloric acid together with a solution of platinic chloride. The chlorides of lithium and sodium give readily soluble double salts with platinic chloride, whilst those of potassium, rubidium, and caesium form double salts which are sparingly soluble. A hundred parts of water at 0° dissolve 0.74 part of potassium platinichloride; the corresponding rubidium platinichloride is only dissolved to the amount of 0.134 part, and the caesium salt, 0.024 part; at 100° are dissolved, 5.13 parts of potassium platinichloride, K_2PtCl_6 , 0.634 part of rubidium platinichloride, and 0.177 part of caesium platinichloride. From this it is clear how the salts of rubidium and caesium may be isolated. The separation of caesium from rubidium by this method is very tedious. It can be better effected by taking advantage of the difference in solubility of their carbonates in alcohol; caesium carbonate, Cs_2CO_3 , is soluble in alcohol, whilst the corresponding salts of rubidium and potassium are almost insoluble. Setterberg separated these metals as alums, but the best method, that given by Scharples, is founded on the fact that from a mixture of the chlorides of potassium, sodium, caesium, and rubidium in the presence of hydrochloric acid, stannic chloride precipitates a double salt of caesium, which is very slightly soluble. The salts of Rb and Cs are closely analogous to those of potassium.

⁴² Bunsen obtained rubidium by distilling a mixture of the tartrate with soot, and Beketoff (1888) by heating the hydroxide with aluminium, $2RbHO + Al = RbAlO_2 + H_2 + Rb$. By the action of 85 grams of rubidium on water, 94,000 heat units are evolved. Setterberg obtained caesium (1882) by the electrolysis of a fused mixture of the cyanides of caesium and barium. Winkler (1890) showed that metallic magnesium reduces the hydrates and carbonates of Rb and Cs like those of the other alkaline metals.

who obtained cæsium by heating CsAlO_2 with Mg.^{42a} According to Eckardt the sp. gr. of Cs=1.88.

Judging by the properties of the free metals, and those of their corresponding and even very complex compounds, lithium, sodium, potassium, rubidium, and cæsium present an indubitable chemical resemblance. The fact that the metals easily decompose water, and that their hydroxides RHO and carbonates R_2CO_3 are soluble in water, whilst the hydroxides and carbonates of nearly all other metals are insoluble, shows that these metals form a natural group of **alkali metals**. The halogens and the alkali metals, with their opposite character, form the two extremes of the elements. Many of the other elements are metals approaching the alkali metals, both in their capacity of forming salts and in not forming acid compounds, but are not so energetic as the alkali metals, that is, they form less energetic bases. Such are the common metals, silver, iron, copper, &c. Some other elements, in the character of their compounds, approach the halogens, and, like them, combine with hydrogen, but these compounds do not show the energetic property of the halogen acids; in a free state they easily

^{42a} Beketoff (1888) showed that metallic aluminium reduces the hydrates of the alkaline metals at a red heat with the formation of aluminates (Chap. XVII.), RAlO_2 —for example, $2\text{KHO} + \text{Al} = \text{KAlO}_2 + \text{K} + \text{H}_2$. It is evident that in this case only half of the alkaline metal is obtained free. On the other hand, K. Winkler (1889) showed that magnesium powder is also able to reduce the alkaline metals from their hydrates and carbonates. N. N. Beketoff and Tscherbacheff (1894) prepared cæsium upon this principle by heating its aluminate CsAlO_2 with magnesium powder: $2\text{CsAlO}_2 + \text{Mg} = \text{MgO}, \text{Al}_2\text{O}_3 + 2\text{Cs}$. We may add that N. N. Beketoff (1887) prepared oxide of potassium, K_2O , by heating the peroxide, KO , in the vapour of potassium, and showed that in dissolving in an excess of water it evolves (for the above-given molecular weight) 67,400 cal. (while 2KHO in dissolving in water evolves 24,920 cal.; so that $\text{K}_2\text{O} + \text{H}_2\text{O}$ gives 42,480 cal.), whence (knowing that $\text{K}_2 + \text{O} + \text{H}_2\text{O}$ in an excess of water evolves 164,500) it follows that $\text{K}_2 + \text{O}$ evolves 97,100 cal. This quantity is somewhat less than that (100,260 cal.) which corresponds to sodium, and the energy of the action of potassium upon water is explained by the fact that K_2O evolves more heat than Na_2O in combining with water (see Chap. II., note 9). Just as hydrogen displaces half the Na from Na_2O , forming NaHO , so also N. N. Beketoff found from experiment and thermo-chemical reasonings that hydrogen displaces half the potassium from K_2O , forming KHO and evolving 7,190 cal. Oxide of lithium, Li_2O , which is easily formed by igniting Li_2CO_3 with carbon (when $\text{Li}_2\text{O} + 2\text{CO}$ is formed), disengages 26,000 cal. with an excess of water, while the reaction $\text{Li}_2 + \text{O}$ gives 114,000 cal. and the reaction $\text{Li}_2 + \text{H}_2\text{O}$ gives only 13,000 cal., and metallic lithium cannot be liberated from oxide of lithium with hydrogen (nor with carbon). Thus in the series Li, Na, K, the formation of R_2O gives most heat with Li and least with K, while the formation of RCl evolves most heat with K (105,000 cal.) and least of all with Li (93,500 cal.). Rubidium, in forming Rb_2O , gives 94,000 cal. (Beketoff). Cæsium, in acting upon an excess of water, evolves 51,500 cal., and the reaction $\text{Cs}_2 + \text{O}$ evolves about 100,000 cal.—i.e., more than K and Rb, and almost as much as Na—and oxide of cæsium reacts with hydrogen (according to the equation, $\text{Cs}_2\text{O} + \text{H} = \text{CsHO} + \text{Cs}$) more easily than any of the oxides of the alkali metals, as was shown by Beketoff (1893). In general Rb and Cs are considered to be even more energetic metals than Na and K.

combine with metals, but they do not then form such saline compounds as the halogens do—in a word, the halogen properties are less sharply defined in them than in the halogens themselves. Sulphur, phosphorus, arsenic, &c. belong to this order of elements. The clearest distinction of the properties of the halogens and alkali metals is expressed in the fact that the former give acids and do not form bases, whilst the latter, on the contrary, only give bases. The first are true **acid elements**, the latter clearly defined **basic or metallic elements**. The first are regarded by those chemists who follow the electrochemical doctrine in one or another form, as being typical electro-negative elements, and the latter as being types of the electro-positive elements. On combining together, the halogens form, in a chemical sense, unstable compounds, and the alkali metals alloys in which the character of the metals remains unaltered, just as in the compound ICl the character of the halogens remains undisguised; thus elements of both classes on combining with members of their own class form non-characteristic compounds, which have the properties of their components. On the other hand, the halogens on combining with the alkali metals form compounds which are, in all respects, stable, and in which the original characters of the halogens and alkali metals have entirely disappeared. The formation of such compounds is accompanied by the evolution of a large amount of heat and by a profound change in both the physical and chemical properties. The alloy of sodium and potassium, although liquid at the ordinary temperature, is perfectly metallic, like both its components. The compound of sodium and chlorine has neither the appearance nor the properties of the original elements; sodium chloride melts at a higher temperature, and is more difficultly volatile, than either sodium or chlorine.

With all these qualitative differences there is, however, an important quantitative **resemblance between the halogens and the alkali metals**. This resemblance is clearly expressed by stating that both orders of elements belong to those which are univalent with respect to hydrogen. It is thus correct to say that both the above-named orders of elements replace hydrogen atom for atom. Chlorine is able to take the place of hydrogen by metalepsis, and the alkali metals take the place of hydrogen in water and acids. As it is possible to consecutively replace every equivalent of hydrogen in a hydrocarbon by chlorine, so also is it possible in an acid containing several equivalents of hydrogen to replace the hydrogen, equivalent by equivalent, by an alkali metal; hence an atom of these elements is analogous to an atom of hydrogen, which is taken, in all cases, as the unit for the comparison of the other elements. In ammonia, and in water, chlorine and sodium are able to

bring about direct replacement. According to the law of substitution, the formation of sodium chloride, NaCl , at once shows the equivalence of the atoms of the alkali metals and the halogens. The halogens and hydrogen and the alkali metals combine with such elements as oxygen, and it is easily proved that in such compounds one atom of oxygen is able to retain two atoms of the halogens, of hydrogen, and of the alkali metals : KHO , K_2O , HClO , and Cl_2O . It must not be forgotten, however, that the halogens give, with oxygen, besides compounds of the type R_2O , higher acid and saline grades of oxidation, which the alkali metals and hydrogen are not capable of forming. We shall soon see (Chap. XV.) that these relations are also subject to a special law, showing a gradual transition of the properties of the elements from the alkali metals to the halogens.

The atomic weights of the alkali metals, lithium 7, sodium 23, potassium 39, rubidium 85, and cæsium 133, show that here, as with the halogens, the elements may be arranged according to their atomic weights in order to compare the properties of the analogous compounds of the members of this group. Thus, for example, the platino-chlorides of lithium and sodium are soluble in water ; those of potassium, rubidium, and cæsium sparingly soluble ; and the greater the atomic weight of the metal the less soluble is the salt. In other cases the reverse is observed—the greater the atomic weight the more soluble are the corresponding salts. The variation of properties with the variation in atomic weight even shows itself in the metals themselves ; thus lithium volatilises with difficulty, whilst sodium is obtained by distillation, potassium volatilises more easily than sodium, and rubidium and cæsium, as we have seen, are still more volatile.

CHAPTER XIV

THE VALENCY AND SPECIFIC HEAT OF THE METALS. MAGNESIUM, CALCIUM, STRONTIUM, BARIUM, AND BERYLLIUM

It is easy, by investigating the composition of corresponding compounds, to establish the **equivalent weights** of the metals compared with hydrogen—that is, the quantity which replaces one part by weight of hydrogen. If a metal decomposes acids directly, with the evolution of hydrogen, the equivalent weight of the metal may be determined by taking a definite weight of it and measuring the volume of hydrogen evolved by its action on an excess of acid; it is then easy to calculate the weight of the hydrogen from its volume.¹ The same result may be arrived at by determining the composition of the normal salts of the metal; for instance, by finding the weight of metal which combines with 35.5 parts of chlorine or 80 parts of bromine.² The equivalent of a metal may be also ascertained by simultaneously (i.e., in one circuit) decomposing an acid and a fused salt of a given metal by an electric current and determining the relation between the amounts of hydrogen and metal separated, because, according to Faraday's law, electrolytes (conductors of the second order) are always decomposed in equivalent quantities.^{2a} The equivalent of a metal may even be found by simply

¹ Under favourable circumstances (by taking all the requisite precautions), the weight of the equivalent may be accurately determined by this method. Thus Reynolds and Ramsay (1887) determined the equivalent of zinc to be 32.7 by this method (from the average of 29 experiments), whilst by other methods it has been fixed (by different observers) between 32.55 and 32.95.

The differences in their equivalents may be demonstrated by taking equal weights of different metals and collecting the hydrogen evolved by them (under the action of an acid or alkali).

² The most accurate determinations of this kind were carried out by Stas, and will be described in Chapter XXIV.

^{2a} The amount of electricity in one ampère-second or one coulomb according to the present nomenclature of electrical units (see works on physics and electro-technology) disengages 0.0001038 gram of hydrogen, 0.001118 gram of silver, 0.0003280 gram of copper from the salts of the oxide, and 0.0006560 gram from the salts of the suboxide. One ampère-hour separates 0.03739 gram of H, 4.0260 grams Ag, 1.323 gram Cl, 0.454 gram Mg, 0.337 gram Al, &c. These amounts stand in the same ratio as the equivalents, i.e., as the quantities replaced by one part by weight of hydrogen. The intimate bond, which is becoming more and more marked, existing between the electrolytic and purely

determining the relation between its weight and that of its salt-giving oxide, as by this we know the quantity of the metal which combines with 8 parts by weight of oxygen, and this will be the equivalent, because 8 parts of oxygen combine with 1 part by weight of hydrogen. One method is verified by another, and the accurate determination of equivalents reduces itself to the discovery of methods for the better separation, isolation, and weighing of the substances under experiment, and hence belongs to the province of analytical chemistry.

For univalent metals, like those of the alkalies, the weight of the equivalent is equal to the weight of the atom. For bivalent metals the atomic weight is equal to the weight of two equivalents, and for n -valent metals it is equal to the weight of n equivalents. Thus aluminium, $\text{Al} = 27$, is trivalent, that is, its equivalent is 9; magnesium, $\text{Mg} = 24$, is bivalent, and its equivalent is 12. Therefore, if potassium or sodium, or in general a univalent metal, M , give compounds M_2O , MHO , MCl , MNO_3 , M_2SO_4 , &c., and in general MX , then for bivalent metals like magnesium or calcium the corresponding compounds will be MgO , $\text{Mg}(\text{HO})_2$, MgCl_2 , $\text{Mg}(\text{NO}_3)_2$, MgSO_4 , &c., or in general MX_2 .

By what are we to be guided in ascribing to some metals univalency and to others bi-, ter-, quadri-, . . . n -valency? What obliges us to make this difference? Why are not all metals given the same valency—for instance, why is not magnesium considered as univalent? If this be done, taking $\text{Mg} = 12$ (and not 24, as now), not only will a simplicity of expression of the composition of all the compounds of

chemical relations of substances (especially in solutions) and the application of electrolysis to the preparation of numerous substances on a large scale, together with the employment of electricity for obtaining high temperatures, &c., makes me regret that the plan and dimensions of this book, and the impossibility of giving a concise and objective exposition of the necessary electrical facts, prevent me from entering upon this province of knowledge, although I consider it my duty to recommend its study to all those who desire to take part in the further development of our science.

There is only one side of the subject respecting the direct correlation between thermo-chemical data and electro-motive force which I think right to mention here, as it justifies the general conception, enunciated by Faraday, that the galvanic current is an aspect of the transference of chemical motion or reaction along the conductors.

From experiments conducted by Favre, Thomsen, Garni, Berthelot, Cheltzoff, and others upon the amount of heat evolved in a closed circuit, it follows that the electro-motive force, E , of the current or its capacity to do a certain work, is *proportional* to the whole amount of heat, Q , disengaged by the reaction forming the source of the current. If E be expressed in volts, and Q in thousands of units of heat referred to equivalent weights, then E will be $0.0436Q$. For example, in a Daniell's battery, $E = 1.09$ both by experiment and theory, because in it there takes place the decomposition of CuSO_4 into $\text{Cu} + \text{O}$ together with the formation of $\text{Zn} + \text{O}$ and $\text{ZnO} + \text{SO}_3\text{Aq}$, and these reactions correspond to $Q = 25.06$ thousand units of heat. So also in all other primary batteries (e.g., Bunsen's, Poggendorff's, &c.) and also in secondary ones (for instance, those acting according to the reaction, $\text{Pb} + \text{H}_2\text{SO}_4 + \text{PbO}_2$, as Cheltzoff showed), $E = 0.0436Q$.

magnesium be attained, but we shall also gain the advantage that their composition will be the same as those of the corresponding compounds of sodium and potassium. These combinations were so expressed formerly—why has this since been changed?

These questions could only be answered after the establishment of the idea of multiples of the atomic weights as the minimum quantities of certain elements combining with others to form compounds—in a word, since the time of the establishment of Avogadro-Gerhardt's law (Chap. VII.). By taking such an element as arsenic, which has many volatile compounds, it is easy to determine the vapour density of these compounds and establish their molecular weights, and hence to find the indubitable atomic weight, exactly as for oxygen, nitrogen, chlorine, carbon, &c. It appears that $\text{As} = 75$, and its compounds correspond, like the compounds of nitrogen, with the forms AsX_3 , and AsX_5 ; for example, AsH_3 , AsCl_3 , AsF_5 , As_2O_5 , &c. It is evident that we are here dealing with an element of two valencies, which, moreover, is never univalent, but ter- or quinque-valent. This example alone is sufficient for the recognition of the existence of polyvalent atoms among the metals.

As we shall see in describing them, there are also many analogous metals among the bivalent elements, some of which also give volatile compounds. For example, zinc, which is itself volatile, gives several volatile compounds (for instance, zinc ethyl, $\text{ZnC}_4\text{H}_{10}$), which boils at 118° , vapour density = 61.3), and in the molecules of all these compounds there is never less than 65 parts of zinc, which is equivalent to H_2 , because 65 parts of zinc displace 2 parts by weight of hydrogen; so that zinc is just such an example of the bivalent metals as oxygen is of the bivalent elements, or as arsenic is of the ter- and quinque-valent elements. And, as we shall afterwards see, magnesium is in many respects closely analogous to zinc, which fact obliges us to regard magnesium as a bivalent metal. Thus the discovery of volatile organo-metallic compounds like zinc-methyl, zinc-ethyl, mercury-ethyl, $\text{Hg}(\text{C}_2\text{H}_5)_2$, &c., and the determination of their vapour densities and reactions present a most important factor in fixing the molecular and atomic weights of many metals. This province of chemistry, which unites inorganic and organic substances, owes much of its development in the middle of the nineteenth century to the indefatigable labours of Sir Edward Frankland, lately deceased, but whose memory will ever remain fresh in our science owing to the light thrown by his numerous researches on many of the most difficult problems of theoretical and applied chemistry.

Such metals as mercury and copper, which are able to give not one

but two bases, are also of particular importance for distinguishing univalent and bivalent metals. Thus copper gives the suboxide Cu_2O and the oxide CuO —that is, the compounds CuX corresponding with the suboxide are analogous (in the quantitative relations, by their composition) to NaX or AgX , and the compounds of the oxide CuX_2 , to MgX_2 , ZnX_2 , and in general to the bivalent metals. It is clear that in such examples we must make a distinction between atomic weights and equivalents.

In this manner the valency, that is, the number of equivalents entering into the atom of a metal, may in many cases be established by means of a few volatile metallic compounds with the aid of a search into their analogies (concerning which see Chap. XV.). **The law of specific heats discovered by Dulong and Petit** has most frequently been applied to the same purpose³ in the history of chemistry, especially since the development given to this law by the researches of Regnault, and since the Italian professor Cannizzaro (1860) showed the agreement between the deductions of this law and the consequences arising from Avogadro-Gerhardt's law.

Dulong and Petit, having determined the specific heat of a number of solid elementary substances, observed that as the atomic weights of

³ The chief means by which we determine the valency of the elements, or what multiple of the equivalent should be ascribed to the atom, are: (1) The law of Avogadro-Gerhardt. This method is the most general and trustworthy, and has already been applied to a great number of elements. (2) The different degrees of oxidation and their isomorphism or analogy in general; for example, $\text{Fe}=56$ because the suboxide (ferrous oxide) is isomorphous with magnesium oxide, &c., and the oxide (ferric oxide) contains half as much oxygen again as the suboxide. Berzelius, Marignac, and others took advantage of this method for determining the composition of the compounds of many elements. (3) The specific heat, according to Dulong and Petit's law. Regnault, and more especially Cannizzaro, used this method to distinguish univalent from bivalent metals. (4) The periodic law (see Chap. XV.) has served as a means for the determination of the atomic weights of cerium, uranium, yttrium, &c. The correction of the results of one method by those of others is generally had recourse to, and is quite necessary, because phenomena of dissociation, polymerisation, &c. may complicate the individual determinations of any one method.

It will be well to observe that a number of other methods, especially from the province of those physical properties which are clearly dependent on the magnitude of the atom (or equivalent) or of the molecule, may lead to the same result. I may point out, for instance, that even the specific gravity of solutions of the metallic chlorides may serve for this purpose. Thus if beryllium be taken as trivalent—that is, if the composition of its chloride be taken as BeCl_3 (or a polymeride of it)—then the specific gravity of solutions of beryllium chloride will not fit into the series of the other metallic chlorides. But by ascribing to it an atomic weight $\text{Be}=7$, or taking Be as bivalent, and the composition of its chloride as BeCl_2 , we arrive at the general rule given in Chapter VII., note 28. Thus W. G. Burdakoff determined in my laboratory that the specific gravity at $15^\circ/4^\circ$ of the solution $\text{BeCl}_2 + 200\text{H}_2\text{O}$ is 1.0138—that is, greater than the corresponding solution $\text{KCl} + 200\text{H}_2\text{O}$ (1.0121), and less than the solution $\text{MgCl}_2 + 200\text{H}_2\text{O}$ (1.0203), as would follow from the magnitude of the molecular weight $\text{BeCl}_2=80$, since $\text{KCl}=74.5$ and $\text{MgCl}_2=95$.

the elements increase, their specific heats decrease, and that *the product of the specific heat Q into the atomic weight A is an almost constant quantity*. This means that to bring different elements into a certain thermal state an equal amount of work is required if atomic quantities of the elements are taken; that is, the amounts of heat expended in heating equal quantities by weight of the elements are far from equal, but are in inverse proportion to the atomic weights. For thermal changes the atom is a unit; all atoms, notwithstanding the difference of weight and nature, are equal. This is the simplest expression of the fact discovered by Dulong and Petit. The specific heat measures that quantity of heat which is required to raise the temperature of *one unit of weight* of a substance by one degree. If the magnitude of the specific heat of elements be multiplied by the atomic weight, then we obtain the **atomic heat**—that is, the amount of heat required to raise the temperature of the atomic weight of an element by one degree. It is these products which for the majority of the elements prove to be approximately, if not quite, identical. A complete identity cannot be expected, because the specific heat of one and the same substance varies with the temperature, with its passage from one state into another, and frequently with even a simple mechanical change of density (for instance, by hammering), not to speak of allotropic changes, &c. We shall cite several figures⁴ proving the truth of the conclu-

⁴ The specific heats here given refer to different limits of temperature, but in the majority of cases between 0° and 100° ; only in the case of bromine the specific heat is taken (for the solid state) at a temperature below -7° , according to Regnault's determination. **The variation of the specific heat with change of temperature** is a very complex phenomenon, the consideration of which I think would here be out of place. I shall only cite a few figures as an example. According to Bystrom, the specific heat of iron at $0^{\circ}=0.1116$, at $100^{\circ}=0.1114$, at $200^{\circ}=0.1188$, at $300^{\circ}=0.1267$, and at $1400^{\circ}=0.4031$. Between these last limits of temperature a change takes place in iron (a spontaneous heating, *recalcescence*), as we shall see in Chap. XXII. For quartz, SiO_2 , Pionchon gives $Q=0.1737+394t10^{-6}-27t^210^{-9}$ up to 400° ; for metallic aluminium (Richards, 1892) at 0° 0.222, at 20° 0.224, at 100° 0.232; consequently, as a rule, the specific heat varies but slightly with the temperature. Still more remarkable are H. E. Weber's observations on the great variation of the specific heat of charcoal, the diamond and boron:

	0°	100°	200°	600°	900°
Wood charcoal	0.15	0.23	0.29	0.44	0.46
Diamond	0.10	0.19	0.22	0.44	0.45
Boron	0.22	0.29	0.35	—	—

These determinations, which have been verified by Dewar, Le Chatelier (Chap. VIII., note 13), Moissan, and Gauthier, the latter finding that for boron, $AQ=6$ at 400° , are of especial importance as confirming the universality of Dulong and Petit's law, because the elements mentioned above form exceptions to the general rule when the mean specific heat is taken for temperatures between 0° and 100° . Thus in the case of the diamond the product of $A \times Q$ at 0° is 1.2, and for boron, 2.4. But if we take the specific heat towards which there is evidently a tendency with a rise of temperature, we obtain

sions arrived at by Dulong and Petit with respect to solid elementary bodies.

	Li	Na	Mg	P
A =	7	23	24	31
Q =	0.9408	0.2934	0.245	0.202
AQ =	6.59	6.75	5.88	6.26
	Fe	Cu	Zn	Br
A =	56	63	65	80
Q =	0.112	0.093	0.093	0.0843
AQ =	6.27	5.86	6.04	6.74
	Pd	Ag	Sn	I
A =	106	108	118	127
Q =	0.0592	0.056	0.055	0.0541
AQ =	6.28	6.05	6.49	6.87
	Pt	Au	Hg	Pb
A =	196	198	200	206
Q =	0.0325	0.0324	0.0333	0.0315
AQ =	6.37	6.41	6.66	6.49

It is seen from this that the product of the specific heat of the element into the atomic weight is an almost constant quantity, which is nearly 6. Hence it is possible to determine the valency by means of the specific heats of the metals. Thus, for instance, the specific

a product approaching to 6 as with other elements. Thus with the diamond and charcoal, it is evident that the specific heat tends towards 0.47, which multiplied by 12 gives 5.6, the same as for magnesium and aluminium. I may here direct the reader's attention to the fact that for solid elements having a small atomic weight the specific heat varies considerably if we take the average figures for temperatures 0° to 100°:

	Li = 7	Be = 9	B = 11	C = 12
Q =	0.94	0.42	0.24	0.20
AQ =	6.6	3.8	2.6	2.4

It is therefore clear that the specific heat of beryllium determined at a low temperature cannot serve for establishing its atomicity. On the other hand, the low atomic heats of charcoal, graphite, and the diamond, boron, &c. may perhaps depend on the complexity of the molecules of these elements. The necessity for acknowledging a great complexity of the molecules of carbon was explained in Chapter VIII. In the case of sulphur the molecule contains at least S_8 and its atomic heat $= 32 \times 0.163 = 5.22$, which is distinctly below the normal. If a large number of atoms of carbon are contained in the molecule of charcoal, this would to a certain extent account for its comparatively small atomic heat. With respect to the specific heat of compounds, it will not be out of place to mention here the conclusion arrived at by Kopp, that the molecular heat (that is, the product of MQ) may be looked on as the sum of the atomic heats of the component elements; but as this rule is not a general one, and can only be applied to give an approximate estimate of the specific heats of substances, I do not think it necessary to go into the details of the conclusions described in Liebig's *Annalen, Supplement-Band*, 1864, which includes a number of determinations made by Kopp.

heats of lithium, sodium, and potassium convince us of the fact that their atomic weights are indeed those which we chose, because by multiplying the specific heats found by experiment by the corresponding atomic weights we obtain Li, 6.59, Na, 6.75, and K, 6.47. Of the alkaline earth metals the specific heats have been determined: that of magnesium = 0.245 (Regnault and Kopp), of calcium = 0.170 (Bunsen), and of barium = 0.05 (Mendeléeff). If the same composition be ascribed to the compounds of magnesium as to the corresponding compounds of potassium, then the equivalent of magnesium will be equal to 12. On multiplying this atomic weight by the specific heat of magnesium, we obtain a figure 2.94, which is half that given by the other solid elements, and therefore the atomic weight of magnesium must be taken as equal to 24 and not to 12. Then the atomic heat of magnesium = $24 \times 0.245 = 5.9$; for calcium, giving its compounds a composition CaX_2 —for example, CaCl_2 , CaSO_4 , CaO ($\text{Ca} = 40$)—we obtain an atomic heat = $40 \times 0.17 = 6.8$, and for barium it is equal to $137 \times 0.05 = 6.85$; that is, they must be regarded as bivalent, so that the atom of each replaces H_2 , Na_2 , or K_2 . This conclusion may be confirmed by a method of analogy, as we shall afterwards see. The application of the principle of specific heats to the determination of the magnitudes of the atomic weights of those metals, the atomic weights of which could not be determined by Avogadro-Gerhardt's law, was made about 1860 by the Italian professor Cannizzaro.

Exactly the same conclusions respecting the bivalence of magnesium and its analogues are obtained by comparing the specific heats of their compounds, especially those of the halogen or most simple compounds, with the specific heats of the corresponding alkali compounds. Thus, for instance, the specific heats of magnesium and calcium chlorides, MgCl_2 and CaCl_2 , are 0.194 and 0.164, and those of sodium and potassium chlorides, NaCl and KCl , 0.214 and 0.172, and therefore their molecular heats (or the products QM , where M is the weight of the molecule) are 18.4 and 18.2, 12.5 and 12.8, and hence the atomic heats (or the quotient of QM by the number of atoms) are all nearly 6, as with the elements. Whilst if, instead of the atomic weights $\text{Mg} = 24$ and $\text{Ca} = 40$, their equivalents 12 and 20 be taken, the atomic heats of the chlorides of magnesium and calcium would then be about 4.6, whilst those of potassium and sodium chlorides are about 6.3.⁵ We must

⁵ It must be remarked that in the case of oxygen (and also hydrogen and carbon) compounds the quotient of MQ/n , where n is the number of atoms in the molecule, is always less than 6 for solids; for example, for $\text{MgO} = 5.0$, $\text{CuO} = 5.1$, $\text{MnO}_2 = 4.6$, ice ($Q = 0.504$) = 3, $\text{SiO}_2 = 3.5$, &c. It is impossible to say whether this depends on the smaller specific heat of the atom of oxygen in its solid compounds (Kopp, note 4) or on

remark, however, that as the specific heat or the amount of heat required to raise the temperature of a unit of weight one degree ⁶ is a complex quantity—including not only the increase of the energy of

some other cause; but, nevertheless, taking into account this decrease depending on the presence of oxygen, a reflection of the atomicity of the elements may to a certain extent be seen in the specific heats of the oxides. Thus for alumina, Al_2O_3 ($Q=0.217$), $MQ=22.3$, and therefore the quotient $MQ/n=4.5$, which is nearly that given by magnesium oxide, MgO . But if we ascribe the same composition to alumina as to magnesia—that is, if aluminium were counted as bivalent—we should obtain the figure 3.7, which is much less. In general, in compounds of identical atomic composition and of analogous chemical properties, the molecular heats MQ are nearly equal, as many investigators have long since remarked. For example, the value for ZnS is 11.7 and for HgS , 11.8; for MgSO_4 , 27.0, and for ZnSO_4 , 28.0, &c.

⁶ If W be the amount of heat contained in a mass m of a substance at a temperature t , and dW the amount expended in heating it from t to $t+dt$, then the specific heat $Q=dW/(m \times dt)$. The specific heat not only varies with the composition and complexity of the molecules of a substance, but also with the temperature, pressure, and physical state of a substance. Even for gases a slight variation of Q with t is to be observed. The constancy of the specific heat of perfect gases forms one of the fundamental propositions of the theory of heat, and on it depends the determination of temperatures by means of gas-thermometers containing hydrogen, nitrogen, or air; but as these give slight differences, it is customary to consider the hydrogen thermometer as normal when the pressure of the gas at 0° is 1,000 mm. of mercury at 0° . Le Chatelier (1887), on the basis of existing determinations, concludes that the molecular heats—that is, the products MQ --of all gases vary in proportion to the temperature, and tend to become equal (6.8) at the absolute zero of temperature (that is, at -273°); and therefore $MQ=6.8+a(273+t)$, where a is a constant quantity increasing with the complexity of the gaseous molecule and Q is the specific heat of the gas under a constant pressure. For permanent gases a almost $=0$, and therefore $MQ=6.8$ —that is, the atomic heat (if the molecule contains two atoms) $=3.4$, as it is in fact (Chap. IX., note 17a). As regards liquids (as well as the vapours formed by them), the specific heat always rises with the temperature. Thus for benzene it equals $0.38+0.0014t$. R. Schiff (1887) showed that the variation of the specific heat of many organic liquids is proportional to the change of temperature (as in the case of gases, according to Le Chatelier), and reduced these variations into dependence upon their composition and absolute boiling-point. It is very probable that the theory of liquids will make use of these simple relations which recall the simplicity of the variation of the specific gravity (Chap. II., note 34), cohesion, and other properties of liquids with the temperature. They are all expressed by the linear function of the temperature, $a+bt$, with the same degree of proximity as the property of gases is expressed by the equation $pv=Rt$.

As regards the relation between the specific heats of liquids (or of solids) and of their vapours, the specific heat of the vapour (and also of the solid) is always less than that of the liquid. For example, the value for benzene vapour is 0.22, and for the liquid, 0.38; for chloroform vapour, 0.13, liquid 0.23; steam 0.475, liquid water 1.0. But the complexity of the relations existing in the specific heat is seen from the fact that the specific heat of ice, 0.0502, is much less than that of liquid water. According to Regnault, in the case of bromine, the specific heat of the vapour $=0.055$ (at 150°), of the liquid $=0.107$ (at 30°), and of solid bromine $=0.084$ (at -15°). One of the problems of the present day is the explanation of those complex relations which exist between the composition and such properties as specific heat, latent heat, expansion by heat, compression, internal friction, cohesion, and so forth. They can only be connected by a complete theory of liquids, which may now soon be expected, more especially as many sides of the subject have already been partially explained.

a substance with its rise in temperature, but also the external work of expansion⁷ and the internal work accomplished in the molecules

⁷ The quantity of heat, Q , required to raise the temperature of one part by weight of a substance by one degree may be expressed by the sum, $Q = K + B + D$, where K is the heat actually expended in heating the substance, or what is termed the absolute specific heat, B the amount of heat expended in the internal work accomplished with the rise of temperature, and D the amount of heat expended in external work. In the case of gases the last quantity may be easily determined, knowing their coefficient of expansion, which is approximately 0.00368. By applying to this case the argument given at the end of note 11, Chapter I., we find that one cubic metre of a gas heated 1° produces external work equal to 10333×0.00368 , or 38.02 kilogram-metres, on which $38.02/424$ or 0.0897 heat unit is expended. This is the heat expended for the external work produced by one cubic metre of a gas, but the specific heat refers to units of weight, and therefore it is necessary to know D in order to reduce the above quantity to a unit of weight. One cubic metre of hydrogen at 0° and 760 mm. pressure weighs 0.0896 kilo, and a gas of molecular weight M has a density $M/2$; consequently a cubic metre weighs (at 0° and 760 mm.) $0.0448M$ kilo, and therefore 1 kilogram of the gas occupies a volume $1/0.0448M$ cubic metres, and the external work D in the heating of 1 kilo of the given gas through $1^\circ = 0.0896/0.0448M$, or $D = 2/M$.

Taking the magnitude of the internal work B for gases as negligible for permanent gases, and therefore supposing $B = 0$, we find the specific heat of gases at a constant pressure, $Q = K + 2/M$, where K is the specific heat at a constant volume, or the true specific heat, and M the molecular weight. Hence $K = Q - 2/M$. The magnitude of the specific heat Q is given by direct experiment. According to Regnault's experiments, for oxygen it = 0.2175, for hydrogen 3.405, and for nitrogen 0.2438; the molecular weights of these gases are 32, 2, and 28, and therefore for oxygen, $K = 0.2175 - 0.0625 = 0.1550$, for hydrogen, $K = 3.4050 - 1.000 = 2.4050$, and for nitrogen, $K = 0.2438 - 0.0714 = 0.1724$. These true specific heats of the elements are in inverse proportion to their atomic weights—that is, their product by the atomic weight is a constant quantity. In fact, for oxygen this product = $0.155 \times 16 = 2.48$, for hydrogen 2.40, for nitrogen $0.1724 \times 14 = 2.414$, and therefore if A stand for the atomic weight we obtain the expression $K \times A = \text{a constant}$, which may be taken as 2.45. This is the true expression of Dulong and Petit's law, because K is the true specific heat and A the weight of the atom. It should be remarked, moreover, that the product of the observed specific heat Q into A is also a constant quantity (for oxygen = 3.48, for hydrogen = 3.40), because the external work D is also inversely proportional to the atomic weight.

In the case of gases we distinguish the specific heat at a constant pressure c' (we designated this quantity above by Q), and that at a constant volume c . It is evident that **the relation between the two specific heats, k** , judging from the above, is the ratio of Q to K , or equal to the ratio of $2.45n + 2$ to $2.45n$. When $n = 1$ this ratio $k = 1.8$; when $n = 2$, $k = 1.4$; when $n = 3$, $k = 1.3$; and with an exceedingly large number, n , of atoms in the molecule, $k = 1$. That is, the ratio between the specific heats decreases from 1.8 to 1.0 as the number of atoms, n , contained in the molecule increases. This deduction is verified to a certain extent by direct experiment. For such gases as hydrogen, oxygen, nitrogen, carbonic oxide, air, and others in which $n = 2$, the magnitude of k is determined by methods described in works on physics (for example, by the change of temperature with an alteration of pressure, by the velocity of sound, &c.), and is found in reality to be nearly 1.4; and for such gases as carbonic anhydride, nitric dioxide, and others it is nearly 1.3. Kundt and Warburg (1875), by means of the approximate method mentioned in note 29, Chapter VII., determined k for mercury vapour when $n = 1$, and found it to be 1.67—that is, a larger quantity than for air, as would be expected from the above.

It may be admitted that the true atomic heat of gases is 2.43 only under the condition that they are distant from a liquid state, and do not undergo a chemical change when heated—that is, when no internal work is produced in them ($B = 0$). Therefore this work may to a certain extent be judged by the observed specific heat. Thus, for instance,

causing them to decompose according to the rise of temperature⁸—it is impossible to expect in the magnitude of the specific heat the great simplicity of relation to composition which we see, for instance, in the density of gaseous substances. Hence, although the specific heat is one of the important means for determining the atomicity of the elements, still the mainstay for a true judgment of atomicity is only given by Avogadro-Gerhardt's law, i.e., the specific heat can only be accessory or preliminary, and when possible, recourse should be had to the determination of the vapour density.

Among the bivalent metals the first place, with respect to their distribution in nature, is occupied by **magnesium** and **calcium**, just as sodium and potassium stand first among the univalent metals. The relation which exists between the atomic weights of these four metals confirms the above comparison. In fact, the combining weight of magnesium is 24, and that of calcium 40; whilst the combining weights of sodium and potassium are 23 and 39—that is, the latter are one unit less than the former.⁹ They all belong to the class of

for chlorine ($Q=0.12$, Regnault; $k=1.33$, according to Straker and Martin, and therefore $K=0.09$, $MK=6.4$), the atomic heat (3.2) is much greater than for other gases containing two atoms in a molecule, and it must be assumed therefore that when it is heated some great internal work is accomplished.

⁸ As an example, it will be sufficient to refer to the specific heat of nitrogen tetroxide, N_2O_4 , which, when heated, gradually passes into NO_2 —that is, chemical work of decomposition proceeds, which consumes heat. Speaking generally, specific heat is a complex quantity, in which it is clear that thermal data (for instance, the heat of reaction) alone cannot give an idea either of chemical or of physical changes individually, but always depend on an association of the one and the other. If a substance be heated from t to t_1 it cannot but suffer a chemical change (that is, the state of the atoms in the molecules changes more or less in one way or another) if dissociation sets in at a temperature t_1 . One gram of hydrogen (specific heat $=3.4$ at a constant pressure) cooled to the temperature of absolute zero will evolve altogether about one thousand units of heat, 8 grams of oxygen about half this amount, whilst in combining together they evolve in the formation of 9 grams of water more than thirty times as much heat. Hence the store of chemical energy (that is, of the motion of the atoms, vortex or other) is much greater than the physical store in the form of heat, but it is the change accomplished by the former that is the cause of chemical transformations. Here we evidently touch on those limits of existing knowledge beyond which the teaching of science does not yet allow us to pass. Many new scientific discoveries have still to be made before this is possible.

⁹ As if $NaH=Mg$ and $KH=Ca$, which is in accordance with their valency. A similar relation (as of Mg to Na or Ca to K) exists between many elements of like atomic weight. I noticed this fact long ago (in 1869, in the first Russian edition of the *Principles of Chemistry*), and it probably has some yet unexplained connection with the general mutual relations of the elements and the periodic system discussed in the following chapter. Professor R. Lorenz turned his attention in 1896 to these twin elements (*Zwillingselemente*), and indicated the following, besides Na and Mg , K and Ca :

$\{ B=11$	$Al=27$	$P=31$	$V=51$	$Mn=55$	$Ni \}$	$=59$
$\{ C=12$	$Si=28$	$S=32$	$Cr=52$	$Fe=56$	$Co \}$	
$\{ Se=79$	$Pd=106.5$	$Sn=119$	$Te \}$	$=127$	$\{ Ta=183$	$Pb=207$
$\{ Br=80$	$Ag=108$	$Sb=120$	$I \}$		$\{ W=184$	$Bi=208$

light metals, as they have but a low specific gravity, in which respect they differ from the ordinary, generally known heavy, or ore, metals (for instance, iron, copper, silver, and lead), which are distinguished by a much greater specific gravity. There is no doubt that their low specific gravity has a significance, not only as a simple point of distinction, but also as a property which determines the fundamental properties of these metals. Indeed, all the light metals have a series of points of resemblance with the metals of the alkalis; thus both magnesium and calcium, like the metals of the alkalis, decompose water (without the addition of acids), although not so easily as the latter metals. The process of the decomposition is essentially one and the same; for example, $\text{Ca} + 2\text{H}_2\text{O} = \text{CaH}_2\text{O}_2 + \text{H}_2$ —that is, hydrogen is liberated and a hydroxide of the metal formed. These hydroxides are bases which neutralise nearly all acids. However, the hydroxides, RH_2O_2 , of calcium and magnesium are in no respect so energetic as those of the true metals of the alkalis; thus when heated they lose water, are not so soluble, develop less heat with acids, and form various salts, which are less stable and more easily decomposed by heat than the corresponding salts of sodium and potassium. For example, calcium and magnesium carbonates easily part with carbonic anhydride when ignited; the nitrates are also very easily decomposed by heat, calcium and magnesium oxides, CaO and MgO , being left behind. The chlorides of magnesium and calcium, when heated with water, evolve hydrogen chloride, forming the corresponding hydroxides, and when ignited yield the anhydrous oxides. All these points are evidence of a weakening of the alkaline properties.

These metals have been termed **the metals of the alkaline earths**, because, like the alkali metals, they form energetic bases. They are called alkaline *earths* because they are met with in nature in a state of

Lorenz also observed that the atomic weights of neighbouring corresponding twin elements differ by 4 (about) or $n \cdot 4$ (about); for instance, $\text{Na} - \text{B} = 20$, $\text{Al} - \text{Na} = 4$, $\text{P} - \text{Al} = 4$, $\text{V} - \text{P} = 20$, &c. Moreover, the difference between the atomicities of the twins is equal to 1 (small, as it should be, according to the periodic law, Chap. XV.); for instance, in the case of K and Ce, B and C, Se and Br, Pb and Bi. However, Lorenz himself saw that this rule is not applicable for many elements, such as H, Be, N, Zn, Ba, Au, and others, and therefore cannot be universally applied. We must moreover direct attention to the fact that the lighter of a pair of twins may have either an odd (for instance, B, Na, Al) or an even (Se, Pd, Sn) atomicity.

In my opinion the above correlations between the magnitudes of the atomic weights of the elements, their analogy and atomicity, as part of those relations which form the essence of the periodic system of the elements (Chap. XV.), can only be explained together with this system, which has the peculiar advantage of giving the possibility of predicting much that has not yet been experimentally observed, while the above-named regularities throw no light upon any fact as yet unknown experimentally. Nevertheless they may have their meaning in the study of the elements, for science is built up of parts and by degrees (Chap. XV., note 12a).³

combination, forming the insoluble mass of the earth, and because as oxides, RO, they themselves have an earthy appearance. Many salts of these metals are known which are insoluble in water, whilst the corresponding salts of the alkali metals are generally soluble—for example, the carbonates, phosphates, borates, and other salts of Mg and Ca are nearly insoluble. This enables us to separate the metals of the alkaline earths from the metals of the alkalies. For this purpose a solution of ammonium carbonate is added to a mixed solution of salts of both groups of metals, when by a double decomposition the insoluble carbonates of the metals of the alkaline earths are formed and fall as a precipitate, whilst the metals of the alkalies remain in solution: $RX_2 + Na_2CO_3 = RCO_3 + 2NaX$.

We may here remark that the oxides of the metals of the alkaline earths are frequently called by special names: MgO is called magnesia or bitter earth, and CaO, lime.

In the primary rocks the lime and magnesia are combined with silica, in variable quantities, in some cases the lime predominating and in other cases the magnesia. The two oxides, being analogous to each other, replace each other in equivalent quantities. The various forms of *augite*, *hornblende* or *amphibole*, and of similar minerals, which enter into the composition of nearly all rocks, contain such compounds of lime and magnesia with silica. The majority of the primary rocks also contain alumina, potash, and soda. These rocks, under the action of water (containing carbonic acid) and air, give up to the water lime and magnesia, which are therefore contained in all kinds of water, and especially in sea water. **The carbonates** $CaCO_3$ and $MgCO_3$, frequently met with in nature, **are soluble in an excess of water saturated with carbonic anhydride**,¹⁰ and therefore many natural waters contain these salts, and are able to yield them when evaporated. However, one kilogram of water saturated with carbonic anhydride under the ordinary pressure does not dissolve more than three grams of calcium carbonate. By gradually expelling the carbonic anhydride from such water an insoluble precipitate of calcium carbonate separates out. It may confidently be stated that the formation of the very widely distributed strata of calcium and magnesium carbonates took place in this way, because these strata are of a sedimentary character—that is, such as would be exhibited by a gradually accumulating deposit on the bottom of the sea, and, moreover, frequently contain the remains of marine plants

¹⁰ Sodium carbonate and other carbonates of the alkalies give acid salts which are less soluble than the normal; here, on the contrary, with an excess of carbonic anhydride, a salt is formed which is more soluble than the normal, but this acid salt is more unstable than sodium hydrogen carbonate, $NaHCO_3$.

and animals, shells, &c. It is very probable that the presence of these organisms in the sea has played the chief part in the precipitation of the carbonates from the sea water, because the plants absorb CO_2 , and many of the organisms CaCO_3 , and after death give deposits of carbonate of lime, for instance, of chalk, which is almost entirely composed of the minute remains of the calcareous shields of such microscopic organisms. These deposits of calcium and magnesium carbonates are the most important sources of these metals. Lime generally predominates, because it is present in rocks and running water in greater quantity than magnesia, and in this case these sedimentary rocks are termed **limestone**. Some of the common flagstones used for paving, &c., and chalk may be taken as examples of this kind of formation. Those limestones in which a considerable portion of the calcium is replaced by magnesium are termed **dolomites**. The dolomites are distinguished by their hardness, and by their not parting with the whole of their carbonic anhydride so easily as the limestones under the action of acids. Dolomites¹¹ sometimes contain an equal number of molecules of calcium and magnesium carbonates, and they also sometimes appear in a crystalline form, which is easily intelligible, because calcium carbonate itself is exceedingly common in this form in nature, and is then known as **calc spar**, whilst natural crystalline magnesium carbonate is termed **magnesite**. The formation of the crystalline varieties of the insoluble carbonates is explained by the possibility of a slow deposition from solutions containing carbonic acid. Besides which (Chap. X.) calcium and magnesium sulphates are obtained from sea water, and therefore they are met with both as deposits and in springs. It must be observed that magnesium is held in considerable quantities in sea water, because the sulphate and chloride of magnesium are very soluble in water, whilst calcium sulphate is but little soluble, and therefore one would expect to find (as actually happens) large masses of calcium sulphate or **gypsum**, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. Gypsum sometimes forms strata of immense size, which extend for many hectometres, for example, in Russia on the Volga, and in the Donetz and Baltic provinces.

¹¹ The formation of dolomite may be explained, if only we imagine that a solution of a magnesium salt acts on calcium carbonate. Magnesium carbonate may be formed by double decomposition, and it must be supposed that this process ceases at a certain limit (Chap. XII.), when we shall obtain a mixture of the carbonates of calcium and magnesium. Haitinger heated a mixture of calcium carbonate, CaCO_3 , with a solution of an equivalent quantity of magnesium sulphate, MgSO_4 , in a closed tube at 200° ; a portion of the magnesia then actually passed into the state of magnesium carbonate, MgCO_3 , and a portion of the lime was converted into gypsum, CaSO_4 . Lubavin (1892) showed that MgCO_3 is more soluble than CaCO_3 in salt water, which is of some significance in explaining the composition of sea water.

Lime and also magnesia, but the latter in much smaller quantities (only to the amount of several fractions of a per cent. and rarely more), enter into **the composition of** every fertile **soil**, and without these bases the soil is unable to support vegetation. Lime is particularly important in this respect, and if absent, its addition to the soil generally improves the harvest, although purely calcareous soils are infertile. For this reason the soil is fertilised both with lime¹² itself and with marl—that is, with clay mixed with a certain quantity of calcium carbonate, strata of which are found nearly everywhere.

From the soil the lime and magnesia (in a smaller quantity) pass into the substance of **plants**, where they occur as salts. Certain of these salts separate in the interior of plants in a crystalline form—for example, calcium oxalate. The lime occurring in plants serves as the source for the formation of the various calcareous secretions which are so common in **animals** of all classes. The bones of the highest animal orders, the shells of mollusca, and the covering of the sea-urchin, contain calcium salts; the shells mainly the carbonate, and the bones mainly the phosphate. Certain limestones are almost entirely formed of such deposits. Odessa is situated on a limestone of this kind, composed of shells. Thus magnesium and calcium occur throughout the entire realm of nature, but calcium predominates.

As lime and magnesia form bases which are in many respects analogous, they were not distinguished from each other for a long time. Although magnesia was obtained in the seventeenth century from Italy, and used as a medicine, it was only in the eighteenth century that Black, Bergmann, and others distinguished it from lime.

Metallic magnesium (and calcium also) is not obtained by heating magnesium oxide or the carbonate with charcoal, as the alkali metals are obtained,¹³ but is liberated by the action of a galvanic current

¹² The undoubted action of lime in increasing the fertility of soils—if not in every case, at all events, with ordinary soils which have long been under corn—is based not so much on the need of plants for the lime itself as on those chemical and physical changes which, as a particularly powerful base, it effects in the mineral and organic elements of the soil.

¹³ Sodium and potassium only decompose magnesium oxide at a white heat and very feebly, probably for two reasons. In the first place, because the reaction $\text{Mg} + \text{O}$ develops more heat (about 140 thousand calories) than $\text{K}_2 + \text{O}$ or $\text{Na}_2 + \text{O}$ (about 100 thousand calories); and, in the second place, because magnesia is not fusible at the heat of a furnace and cannot act on the charcoal, sodium, or potassium—that is, it does not pass into that mobile state which is necessary for reaction. The first reason alone is not sufficient to explain the absence of the reaction between charcoal and magnesia, because iron and charcoal in combining with oxygen evolve less heat than sodium or potassium, yet, nevertheless, they can displace them. With respect to magnesium chloride, it acts on sodium and potassium, not only because their combination with chlorine evolves more heat than the combination of chlorine and magnesium ($\text{Mg} + \text{Cl}_2$ gives 150 and $\text{Na}_2 + \text{Cl}_2$ about 195 thousand calories), but also because a fusion, both of the magnesium chloride

on fused magnesium chloride (best mixed with potassium chloride) Davy and Bussy obtained metallic magnesium by acting on magnesium chloride with the vapour of potassium. According to Deville's process magnesium was prepared in moderately large quantities by a similar process, only the potassium is replaced by sodium. Anhydrous magnesium chloride, together with sodium chloride and calcium fluoride, is fused in a closed crucible. The latter substances only serve to facilitate the formation of a fusible mass before and after the reaction, which is indispensable in order to prevent the access and action of air. One part of finely divided sodium to five parts of magnesium chloride is thrown into the strongly heated molten mass, and after stirring, the reaction proceeds very quickly, and magnesium separates: $\text{MgCl}_2 + \text{Na}_2 = \text{Mg} + 2\text{NaCl}$. In working on a large scale, the powdery metallic magnesium is then subjected to distillation at a white heat. The distillation of the magnesium is necessary, because the undistilled metal is not homogeneous¹⁴ and burns unevenly: the metal is chiefly prepared for the purpose of illumination. Magnesium is now prepared on a large scale by the action of an electric current upon calcined and molten carnallite, the double salt of MgCl_2 and KCl . The current first decomposes the MgCl_2 and deposits metallic magnesium on the cathode (the walls of the iron crucible in which the salt is melted) in a molten state. In the laboratory this may be done on a small scale in a common clay pipe. Magnesium is a white metal, like silver, of sp. gr. 1.75; it is not soft like the alkali metals, but is, on the contrary, hard like the majority of the ordinary metals. This follows from the fact that it melts at a somewhat high temperature—above 500° —and boils at about 1000° . It is malleable and ductile, like the generality of metals, so that it can be drawn into wires and rolled into ribbon; it is most frequently used for lighting purposes in the latter form. Unlike the alkali metals, magnesium does not decompose the atmospheric moisture at the ordinary temperature, so that it is almost unacted on by air; it is not even acted on by water at the ordinary temperature, so that it may be washed to free it from

and of the double salt, takes place under the action of heat. It is probable, however, that a reverse reaction will take place. A reverse reaction might probably be expected, and Winkler (1890) showed that Mg reduces the oxides of the alkali metals (Chap. III., note 42).

¹⁴ Commercial magnesium generally contains a certain amount of *magnesium nitride* (Deville and Caron), Mg_3N_2 , which is a product of substitution of ammonia directly formed (as is easily shown by experiment) when magnesium is heated in nitrogen. It is a yellowish-green powder, which gives ammonia and magnesia with water, and cyanogen when heated with carbonic anhydride. Pashkoffsky (1893) showed that Mg_3N_2 is easily formed and is the sole product when Mg is heated to redness in a current of NH_3 . Purer magnesium may be obtained by the action of a galvanic current.

sodium chloride. Magnesium only decomposes water with evolution of hydrogen at the boiling-point of water.¹⁵ This is explained by the fact that in decomposing water magnesium forms an insoluble hydroxide, MgH_2O_2 , which covers the metal and hinders the further action of the water. Magnesium easily displaces hydrogen from acids, forming magnesium salts. When ignited it **burns** not only in oxygen but in air (and even in carbonic anhydride), forming a white powder of magnesium oxide, or magnesia; in burning it emits a white and exceedingly **brilliant light**. The strength of this light naturally depends on the fact that magnesium (24 parts by weight) in burning evolves about 140 thousand heat units, and that the product of combustion, MgO , is infusible by heat; so that the vapour of the burning magnesium contains an ignited powder of non-volatile and infusible magnesia, and consequently presents all the conditions for the production of a brilliant light. The light emitted by burning magnesium contains many rays which act chemically, and are situated in the violet and ultra-violet parts of the spectrum. For this reason burning magnesium may be employed for producing even instantaneous photographic images.¹⁶

Owing to its great affinity for oxygen, magnesium **reduces** many metals (zinc, iron, bismuth, antimony, cadmium, tin, lead, copper, silver, and others) from solutions of their salts at the ordinary temperature,¹⁷ and at a red heat finely divided magnesium takes up the oxygen from silica, alumina, boric anhydride, &c.; so that silicon (and many other elements) may be obtained by directly heating a mixture of powdered silica and magnesium in an infusible glass tube.¹⁸

The affinity of magnesium for the halogens is much more feeble than for oxygen,¹⁹ as is at once evident from the fact that a solution

¹⁵ Hydrogen peroxide (Weltzien) dissolves magnesium. The reaction, as far as I know, has not been investigated, but probably a compound of Mg and H_2O_2 is formed.

¹⁶ A special form of apparatus is used for burning magnesium. It is a clockwork arrangement containing a rotating cylinder round which a ribbon or wire of magnesium is wound. The wire is subjected to a uniform unwinding and burning as the cylinder rotates, and in this manner the combustion may continue uniform for a certain time. The same is attained in special lamps, by causing a mixture of sand and finely divided magnesium to fall from a funnel-shaped reservoir on to the flame. In photography it is best to blow finely divided magnesium into a colourless (spirit or gas) flame, and for instantaneous photography to light a cartridge of a mixture of magnesium and chlorate of potassium by means of a spark from a Ruhmkorff's coil (V. D. Mendeléef, 1889).

¹⁷ According to the observations of Maack, Comaille, Böttger, and others. The reduction by heat mentioned further on was pointed out by Geuther, Phipson, Parkinson, and Gattermann.

¹⁸ This action of metallic magnesium depends on its volatility, and on the fact that, in combining with a given quantity of oxygen, it evolves more heat than aluminium, silicon, potassium, and other elements.

¹⁹ Davy, on heating magnesia in chlorine, concluded that there was a complete

of iodine acts feebly on magnesium ; still, magnesium burns in the vapours of iodine, bromine, and chlorine. The character of magnesium is also seen in the fact that all its salts, especially in the presence of water, are decomposable at a comparatively moderate temperature, the elements of the acid being evolved, and the magnesium oxide, which is non-volatile and unchangeable by heat, being left. This naturally refers to those acids which are themselves volatilised by heat. Even magnesium sulphate is completely decomposed at the temperature at which iron melts, oxide of magnesium remaining behind. This decomposition of magnesium salts by heat proceeds much more easily than that of calcium salts. For example, magnesium carbonate is totally decomposed at 170° , magnesium oxide being left behind. This **magnesia**, or **magnesium oxide**, is met with both in an anhydrous and hydrated state in nature (the anhydrous magnesia as the mineral *periclase*, MgO , and the hydrated magnesia as *brucite*, MgH_2O_2). Magnesia is a well-known medicine (calcined magnesia—*magnesia usta*). It is a white, extremely fine, and very voluminous powder, of specific gravity 3.4 ; it is infusible at a furnace heat, and only shrinks or shrivels in an oxyhydrogen flame. After long contact, anhydrous magnesia combines with water, although very slowly, forming the hydroxide $\text{Mg}(\text{HO})_2$, which, however, when heated even below a red heat, parts with its water with great ease, again yielding anhydrous magnesia. This hydroxide is obtained directly as a gelatinous amorphous substance when a soluble alkali is mixed with a solution of any magnesium salt, $\text{MgCl}_2 + 2\text{KHO} = \text{Mg}(\text{HO})_2 + 2\text{KCl}$. This decomposition is complete, and nearly all the magnesium passes into the precipitate, indicating clearly the almost perfect insolubility of magnesia in water. Water dissolves a scarcely perceptible quantity of magnesium hydroxide—of which, indeed, one part is dissolved by 55,000 parts of water, and yet the solution has an alkaline reaction, and gives, with a salt of phosphoric acid, a precipitate of magnesium phosphate, which is still more insoluble. Magnesia is not only dissolved by acids, forming salts, but it also displaces certain other bases—for example, ammonia from ammonium salts when boiled ; and the hydroxide also absorbs carbonic anhydride from the air. The magnesium salts, like those of calcium, potassium, and sodium, are colourless if they are formed from colourless acids. Those which are soluble have a bitter taste, whence magnesia has been termed **bitter-earth**. In comparison with the alkalis, magnesia is a feeble base, inasmuch as it forms somewhat unstable

substitution, because the volume of the oxygen was half that of the chlorine ; it is probable, however, that owing to the formation of chlorine oxide (Chap. XI., note 30) the decomposition is not complete, and is limited by a reverse reaction.

salts, easily gives basic salts, forms acid salts with difficulty, and is able to give double salts with the salts of the alkalies; which facts are characteristic of feeble bases, as we shall see in becoming acquainted with the different metals.

The power of magnesium salts to form **double** and basic **salts** is very frequently shown in its reactions, and is specially marked as regards **ammonium salts**. If saturated solutions of magnesium and ammonium sulphates are mixed together, a crystalline double salt $\text{Mg}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$,²⁰ is immediately precipitated. A strong solution of ordinary ammonium carbonate dissolves magnesium oxide or carbonate, and precipitates crystals of a double salt, $\text{Mg}(\text{NH}_4)_2(\text{CO}_3)_2 \cdot 4\text{H}_2\text{O}$, from which water extracts the ammonium carbonate. With an excess of an ammonium salt the double salt passes into solution,²¹ and therefore if a solution contain a magnesium salt and an excess of an ammonium salt—for instance, sal-ammoniac—sodium carbonate will no longer precipitate magnesium carbonate. A mixture of solutions of magnesium and ammonium chlorides, on evaporation or refrigeration, gives a double salt, $\text{Mg}(\text{NH}_4)\text{Cl}_3 \cdot 6\text{H}_2\text{O}$.²² The salts of potassium, like those of ammonium, are able to enter into combination with magnesium salts.²³ For instance, the double salt, $\text{MgKCl}_3 \cdot 6\text{H}_2\text{O}$, which is known as **carnallite**,²⁴ and occurs in the salt

²⁰ Even a solution of ammonium chloride gives this salt with magnesium sulphate. Its sp. gr. is 1.72; 100 parts of water at 0° dissolve 9, and at 20° 17.9 parts of the anhydrous salt. At about 130° it loses all its water.

²¹ This is an example of equilibrium and of the influence of mass; the double salt is decomposed by water; but if, instead of water, we take a solution of that soluble part which is formed in the decomposition of the double salt, the latter dissolves as a whole.

²² If an excess of ammonia be added to a solution of magnesium chloride, only half of the magnesium will be thrown down in the precipitate: $2\text{MgCl}_2 + 2\text{NH}_4\text{OH} = \text{Mg}(\text{OH})_2 + \text{Mg} \cdot \text{NH}_4\text{Cl}_3 + \text{NH}_4\text{Cl}$. A solution of ammonium chloride reacts with magnesia, evolving ammonia and forming a solution of the same salt: $\text{MgO} + 3\text{NH}_4\text{Cl} = \text{MgNH}_4\text{Cl}_3 + \text{H}_2\text{O} + 2\text{NH}_3$.

Among the double salts of ammonium and magnesium, the phosphate, $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$, is almost insoluble in water (0.07 gram is soluble in a litre), even in the presence of ammonia. Magnesia is very frequently precipitated as this salt from solutions in which it is held by ammonium salts. As lime is not retained in solution by the presence of ammonium salts, but is nevertheless precipitated by sodium carbonate, &c., it is very easy to *separate* calcium from magnesium by taking advantage of these properties.

²³ In order to see the nature and cause of formation of double salts, it is sufficient (although this does not embrace the whole essence of the matter) to consider that one of the metals of such salts (for instance, potassium) easily gives acid salts, and the other (in this instance, magnesium) basic salts; the properties of distinctly basic elements predominate in the former, whilst in the latter these properties are enfeebled, and the salts formed by them bear the character of acids—for example, the salts of aluminium or magnesium act in many cases like acids. By their mutual combination these two opposite properties of the salts are, as it were, both satisfied.

²⁴ Carnallite has been mentioned in Chap. X. (note 4) and in Chap. XIII. These deposits also contain much *kainite*, $\text{KMgCl}(\text{SO}_4) \cdot 3\text{H}_2\text{O}$ (sp. gr. 2.13; 100 parts of water

mines of Stassfurt, may be formed by freezing a saturated solution of potassium chloride with an excess of magnesium chloride. A saturated solution of magnesium sulphate dissolves potassium sulphate, and solid magnesium sulphate is soluble in a saturated solution of potassium sulphate. A double salt, $\text{K}_2\text{Mg}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, which closely resembles the above-mentioned ammonium salt, crystallises from these solutions; ²⁵

dissolve 79.6 parts at 18°. This double salt contains two metals and two haloids. Feit (1889) also obtained a bromide corresponding to carnallite.

²⁵ The component parts of certain double salts diffuse at different rates, and as the diffused solution contains a different proportion of the component salts than the solution of the double salt taken, it seems as if such salts are decomposed by water. According to Rüdorff, the double salts, like carnallite, $\text{MgK}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, and the alums, all belong to this order (1888). But such salts as tartar emetic, the double oxalates, and double cyanides are not separated by diffusion, which in all probability depends both on the relative rate of the diffusion of the component salts and on the degree of affinity acting between them. Those complex states of equilibrium which exist between water, the individual salts, MX and NY, and the double salt, MNXY, have been already partially analysed (as will be shown hereafter) in that case when the system is heterogeneous (that, is, when something separates out in a solid state from the liquid solution); but in the case of equilibrium in a homogeneous liquid medium (in a solution) the phenomenon is not so clear, because it concerns that very theory of solution which cannot yet be considered as established (Chap. I., note 9, and others). As regards the heterogeneous decomposition of double salts, it has long been known that such salts as carnallite and $\text{K}_2\text{Mg}(\text{SO}_4)_2$ give up the more soluble salt if an insufficient quantity of water for their complete solution be taken, i.e., water decomposes the double salt. The complete saturation of 100 parts of water requires at 0° 14.1, at 20° 25, and at 60° 50.2 parts of the latter double salt (anhydrous), while 100 parts of water dissolve 27 parts of magnesium sulphate at 0°, 36 parts at 20°, and 55 parts at 60°, if the anhydrous salt is taken (note 27). Of all the states of equilibrium exhibited by double salts the most fully investigated as yet is the system containing water, sodium sulphate, magnesium sulphate, and their double salt, $\text{Na}_2\text{Mg}(\text{SO}_4)_2$, which crystallises with 4 and 6 mols. of H_2O . The first crystallhydrate, $\text{MgNa}_2(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, occurs at Stassfurt, and as a sedimentary deposit in many of the salt lakes near Astrakhan, and is therefore called **astrakhanite**. The specific gravity of the monoclinic prisms of this salt is 2.22. If this salt, in a finely divided state, is mixed with the necessary quantity of water [according to the equation $\text{MgNa}_2(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O} + 13\text{H}_2\text{O} = \text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} + \text{MgSO}_4 \cdot 7\text{H}_2\text{O}$], the mixture solidifies like plaster of Paris into a homogeneous mass if the temperature is *below* 22° (van't Hoff and van Deventer, 1886; Bakhuis Roozeboom, 1887); but if the temperature be above this *transition-point* the water and double salt will not react on each other, that is, they will not solidify nor give a mixture of sodium and magnesium sulphates. If a mixture (in equivalent quantities) of solutions of these salts be evaporated, and crystals of astrakhanite and of the individual salts capable of proceeding from it be added to the concentrated solution to avoid the possibility of a supersaturated solution, then at temperatures above 22° astrakhanite will be exclusively formed (this is the method of its production); but at lower temperatures the individual salts are alone produced. If equivalent amounts of Glauber's salt and magnesium sulphate be mixed together in a solid state, there is no change at temperatures below 22°, but at higher temperatures astrakhanite and water are formed. The volume occupied by $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ in grams is $322 \cdot 146 = 220.5$ cubic centimetres, and by $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, $246/1.68$ or 146.4 c.c.; hence their mixture in equivalent quantities occupies a volume of 366.9 c.c. The volume of astrakhanite is $334 \cdot 222$ or 150.5 c.c., and the volume of $13\text{H}_2\text{O}$, 234 c.c.; hence their sum is 380.5 c.c., and therefore it is easy to follow the formation of the astrakhanite in a suitable apparatus (a kind of thermometer containing oil and a powdered mixture of sodium and magnesium sulphates),

it occurs as the mineral **kainite** at Stassfurt. The nearest analogues of magnesium are able to give double salts exactly similar to this, both in crystalline form (monoclinic system) and composition; like this salt (see Chap. XV.), they are able (at 140°) to part easily with all their water of crystallisation, and correspond with the salts of sulphuric acid, whose type may be taken as **magnesium sulphate**, MgSO_4 .²⁶ It occurs at Stassfurt as *kieserite*, $\text{MgSO}_4 \cdot \text{H}_2\text{O}$, and generally separates from solutions as a heptahydrated salt, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, and from supersaturated

and to see by the variation in volume that below 22° it remains unchanged, and, when heated, proceeds the more quickly, the higher the temperature. At the transition temperature the solubility of astrakhanite and of the mixture of the component salts is one and the same, whilst at higher temperatures a solution which is saturated for a mixture of the individual salts would be supersaturated for astrakhanite, and at lower temperatures the solution of astrakhanite will be supersaturated for the component salts, as has been shown in great detail by Karsten, Deacon, and others. Roozeboom showed that there are two limits to the composition of the solutions which can exist for a double salt: these limits are respectively obtained by dissolving a mixture of the double salt with each of its component simple salts. Van't Hoff demonstrated, besides this, that the tendency towards the formation of double salts has a distinct influence on the progress of double decomposition, for at temperatures above 31° the mixture, $2\text{MgSO}_4 \cdot 7\text{H}_2\text{O} + 2\text{NaCl}$ passes into $\text{MgNa}_2(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O} + \text{MgCl}_2 \cdot 6\text{H}_2\text{O} + 4\text{H}_2\text{O}$, whilst below 31° there is not this double decomposition, but it proceeds in the opposite direction, as may be demonstrated by the above-described methods. Van der Heyd obtained a potassium astrakhanite, $\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 4\text{H}_2\text{O}$, from solutions of the component salts at 100° .

From these experiments on double salts we see that there is as close a dependence between the temperature and the formation of substances as there is between the temperature and a change of state. It is a case of Deville's principles of dissociation, extended in the direction of the passage of a solid into a liquid. On the other hand, we see here how essential a rôle water plays in the formation of compounds, and how the affinity for water of crystallisation is essentially analogous to the affinity between salts, and hence also to the affinity of acids for bases, because the formation of double salts does not differ in any essential point (except the degree of affinity—that is, only quantitatively) from the formation of salts themselves. When sodium hydroxide with nitric acid gives sodium nitrate and water, the phenomenon is essentially the same as in the formation of astrakhanite from the salts $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ and $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$. Water is disengaged in both cases, and hence the volumes are altered. In these remarks, which chiefly concern astrakhanite, I wish to give an example of that class of chemical research which is now most often treated by means of the so-called phase rule, whose greatest value consists in giving a graphical representation of the complex relations encountered here. Several other instances also serve as examples of the application of this method, and in speaking of FeCl_3 (Chap. XXII.) an example of the graphical representation of the phenomena is given. Further details must be looked for in works on physical and theoretical chemistry.

²⁶ This salt, and especially its crystallo-hydrate with $7\text{H}_2\text{O}$, is generally known as Epsom salts. It has long been used as a purgative. It is easily obtained from magnesia and sulphuric acid, and it separates on the evaporation of sea water and of many saline springs. When carbonic anhydride is obtained by the action of sulphuric acid on magnesite, magnesium sulphate remains in solution. When dolomite—that is, a mixture of magnesium and calcium carbonates—is subjected to the action of a solution of hydrochloric acid until about half of the salt remains, the calcium carbonate is mostly dissolved and magnesium carbonate left in the residue, which, by treatment with sulphuric acid, gives a solution of magnesium sulphate.

solutions as a hexahydrated salt, $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$; at temperatures below 0° it crystallises out as a dodecahydrated salt, $\text{MgSO}_4 \cdot 12\text{H}_2\text{O}$, and a solution of approximately the composition $\text{MgSO}_4 \cdot 24\text{H}_2\text{O}$ solidifies completely at -5° .²⁷ Thus between water and magnesium sulphate there may exist several definite and more or less stable degrees of equilibrium; the double salt, $\text{MgSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$, may be regarded as one of these equilibrated systems, the more so since it contains $6\text{H}_2\text{O}$, whilst MgSO_4 forms its most stable system with $7\text{H}_2\text{O}$, and the double salt

²⁷ The anhydrous salt, MgSO_4 (sp. gr. 2.61), attracts moisture (7 mol. H_2O) from moist air; when heated in steam or hydrogen chloride it gives sulphuric acid, and when heated with carbon it is decomposed according to the equation, $2\text{MgSO}_4 + \text{C} = 2\text{SO}_2 + \text{CO}_2 + 2\text{MgO}$. The monohydrated salt (kieserite), $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ (sp. gr. 2.56), dissolves in water with difficulty: it is formed by heating the other crystallo-hydrates to 135° . The hexahydrated salt is dimorphous. If a solution, saturated at the boiling-point, is prepared, and cooled without access of crystals of the heptahydrated salt, $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ crystallises out in *monoclinic* prisms (Loewel, Marignac), which are quite as unstable as the salt, $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$; but if prismatic crystals of the cubic system of the copper-nickel salts of the composition $\text{MSO}_4 \cdot 6\text{H}_2\text{O}$ be added, then crystals of $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ are deposited on them as prisms of the *cubic* system (Lecoq de Boisbaudran). The ordinary crystallo-hydrate, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, Epsom salts, belongs to the *rhombic* system, and is obtained by crystallisation below 30° . Its specific gravity is 1.69. In a vacuum, or at 100° , it loses $5\text{H}_2\text{O}$, at 132° $6\text{H}_2\text{O}$, and at 210° the whole of the $7\text{H}_2\text{O}$ (Graham). If crystals of ferrous or cobaltic sulphate be placed in a saturated solution, *hexagonal* crystals of the heptahydrated salt are formed (Lecoq de Boisbaudran); they present an unstable state of equilibrium, and soon become cloudy, probably owing to their transformation into the more stable common form. Fritzsche, by cooling saturated solutions below 0° , obtained a mixture of crystals of ice and of a dodecahydrated salt which easily split up at temperatures above 0° . Guthrie showed that dilute solutions of magnesium sulphate, when refrigerated, separate ice until the solution attains a composition $\text{MgSO}_4 \cdot 24\text{H}_2\text{O}$, which will completely freeze into a crystallo-hydrate at -5.3° . According to Coppet and Rüdorff, the temperature of the formation of ice falls by 0.073° for every part by weight of the heptahydrated salt per 100 of water. This figure gives (Chap. I., note 49) $i = 1$ for both the heptahydrated and the anhydrous salt, from which it is evident that it is impossible to judge of the state of combination in which a dissolved substance occurs by the temperature of the formation of ice.

The solubility of the different crystallo-hydrates of magnesium sulphate, according to Loewel, also varies, like those of sodium sulphate or carbonate (see Chap. XII., notes 7 and 18). At 0° 100 parts of water dissolves 40.75 MgSO_4 in the presence of the hexahydrated salt, 34.67 MgSO_4 in the presence of the hexagonal heptahydrated salt, and only 26 parts of MgSO_4 in the presence of the ordinary heptahydrated salt—that is, solutions giving the remaining crystallo-hydrates will be supersaturated for the ordinary heptahydrated salt.

All this shows how many diverse aspects of more or less stable equilibria may exist between water and a substance dissolved in it; this has already been enlarged on in Chap. I.

Carefully purified magnesium sulphate in its aqueous solution gives, according to Stcherbakoff, an alkaline reaction with litmus, and an acid reaction with phenolphthalein.

The specific gravities of solutions of certain salts of magnesium and calcium reduced to $15^\circ/4^\circ$ (see my work cited, Chap. I., note 19) are, if water at $4^\circ = 10,000$ —

$$\text{MgSO}_4 : s = 9,992 + 99.89p + 0.553p^2$$

$$\text{MgCl}_2 : s = 9,992 + 81.31p + 0.372p^2$$

$$\text{CaCl}_2 : s = 9,992 + 80.24p + 0.476p^2$$

may be considered as this crystallo-hydrate in which one molecule of water is replaced by the molecule K_2SO_4 .²⁸

The power of forming basic salts is a very remarkable peculiarity of magnesia and other feeble bases, and especially of those corresponding with polyvalent metals. The very powerful bases corresponding with univalent metals—like potassium and sodium—do not form basic salts, and, indeed, are more prone to give acid salts, whilst magnesium easily and frequently forms basic salts, especially with feeble acids, although there are some oxides—as, for example, copper and lead oxides—which still more frequently give basic salts. If a cold solution of magnesium sulphate is mixed with a solution of sodium carbonate there is formed a gelatinous precipitate of a basic salt, $Mg(OH)_2, 4MgCO_3, 9H_2O$; but all the magnesia is not precipitated in this case, as a portion of it remains in solution as an acid double salt. If sodium carbonate be added to a boiling solution of magnesium sulphate, a precipitate of a still more basic salt is formed, thus: $4MgSO_4 + 4Na_2CO_3 + 4H_2O = 4Na_2SO_4 + CO_2 + Mg(OH)_2, 3MgCO_3, 3H_2O$. This basic salt forms the ordinary drug **magnesia** (*magnesia alba*), usually in the form of light porous lumps. Other basic salts are formed under certain modifications of temperature and conditions of decomposition. But **the normal salt**, $MgCO_3$, which occurs in nature as magnesite in the form of rhombohedra of specific gravity 3.056, is not then obtained. In fact, the formation of the different basic salts shows the power of water to decompose the normal salt. It is possible, however, to obtain this salt in both an anhydrous and hydrated state. A solution of magnesium carbonate in water containing carbonic acid is taken for this purpose. The reason for this is easily understood, carbonic anhydride being one of the products of the decomposition of magnesium carbonate in the presence of water. If this solution is left to evaporate spontaneously the normal salt separates in a hydrated form, but on the evaporation of a heated solution, through which a stream of carbonic anhydride is passed, the anhydrous salt is formed as a crystalline mass, which remains unaltered in the air, like the natural mineral.²⁹ The decomposing influence of water on the salts of magnesium, which is

²⁸ Graham even distinguished the last equivalent of the water of crystallisation of the heptahydrated salt as that which is replaced by other salts, pointing out that double salts like $MgK_2(SO_4)_2, 6H_2O$ lose all their water at 135° , when $MgSO_4, 7H_2O$ only parts with $6H_2O$.

²⁹ The crystalline form of the anhydrous salt obtained in this manner is not the same as that of the natural salt. The former gives rhombohedra, like those in which calcium carbonate appears as calc spar, whilst the natural salt appears in the form of rhombic prisms, similar to those sometimes presented by the same carbonate as aragonite, which will shortly be described.

directly dependent on the feeble basic properties of magnesia,³⁰ is most clearly seen with **magnesium chloride**, MgCl_2 . This salt is contained³¹ in the last mother liquors of the evaporation of sea water. On cooling a sufficiently concentrated solution, the crystallo-hydrate, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, separates;³² but if it is further heated (above 106°) to remove the water, hydrochloric acid begins to pass off together with the latter, so that there ultimately remains magnesia with a small quantity of magnesium chloride.³³ From what has been said it is evident that anhydrous magnesium chloride cannot be obtained by simple evaporation. But if sal-ammoniac or sodium chloride be added to a solution of magnesium chloride, the evolution of hydrochloric acid does not then take place, and after complete evaporation the residue is perfectly soluble in water. This renders it possible to obtain anhydrous magnesium chloride from its aqueous solution. Indeed, the mixture with sal-

³⁰ Magnesium sulphate enters into certain reactions which are proper to sulphuric acid itself. Thus, for instance, if a carefully prepared mixture of equivalent quantities of hydrated magnesium sulphate and sodium chloride is heated to redness, the evolution of hydrochloric acid is observed just as in the action of sulphuric acid on common salt: $\text{MgSO}_4 + 2\text{NaCl} + \text{H}_2\text{O} = \text{Na}_2\text{SO}_4 + \text{MgO} + 2\text{HCl}$. Magnesium sulphate acts in a similar manner on nitrates, with the evolution of nitric acid. A mixture of it with common salt and manganese peroxide gives chlorine. Sulphuric acid is sometimes replaced by magnesium sulphate in galvanic batteries—for example, in the well-known Meidinger battery. In the above-mentioned reactions we see a striking example of the similarity of the reactions of acids and salts, especially those of the latter containing such feeble bases as magnesia.

³¹ As sea-water contains many salts, MCl and MgX_2 , it follows, according to Berthollet's teaching, that MgCl_2 is also present.

³² As the crystallo-hydrates of the salts of sodium often contain $10\text{H}_2\text{O}$, so many of the salts of magnesium contain $6\text{H}_2\text{O}$. However, MgCl_2 also combines with H_2O in other proportions in definite crystallo-hydrates, according to the temperature. This subject has been fully studied by van't Hoff and Meyerhoffer (1898), who showed the formation of crystallo-hydrates with 8 (at -17°) and $12\text{H}_2\text{O}$ (at -32°) below 0° , whilst above 0° those with 6 (at 116.7°), and $2\text{H}_2\text{O}$ (above 181°) are formed. The last of these crystallo-hydrates, $\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$, was obtained by Ditte, by passing HCl into a saturated solution of MgCl_2 and evaporating the residue in a stream of HCl at -140 . The solubility of MgCl_2 is as follows: 100 grams of water dissolve 52.2 grams of the salt at 0° , 57.9 grams at 25° and 65.8 grams at 80° .

³³ This decomposition is most simply defined as the result of the two reverse reactions, $\text{MgCl}_2 + \text{H}_2\text{O} = \text{MgO} + 2\text{HCl}$ and $\text{MgO} + 2\text{HCl} = \text{MgCl}_2 + \text{H}_2\text{O}$, or as a distribution between O and Cl_2 on the one hand and H_2 and Mg on the other. It is then clear that, according to Berthollet's doctrine, the mass of the hydrochloric acid converts the magnesium oxide into chloride, whilst the mass of the water converts the magnesium chloride into oxide. On mixing ignited magnesia with a solution of magnesium chloride of specific gravity about 1.2, a solid mass is obtained which is scarcely decomposed by water at the ordinary temperature (see Chap. XVI., note 4). A similar means is employed for cementing sawdust into a solid mass, called xylolite, used for flooring, &c.

We may remark that MgBr_2 crystallises not only with $6\text{H}_2\text{O}$ (temperature of fusion 152°), but also with $10\text{H}_2\text{O}$ (temperature of fusion $+12^\circ$, formed at -18° . Panfiloff, 1894).

ammoniac (in excess) may be dried (the residue consists of an anhydrous double salt, $\text{MgCl}_2 \cdot 2\text{NH}_4\text{Cl}$) and then ignited (460°), when the sal-ammoniac is converted into vapour, and a fused mass of anhydrous magnesium chloride remains behind. The anhydrous chloride evolves a very considerable amount of heat on the addition of water,³⁴ Anhydrous magnesium chloride is not only obtained by the above method, but is also formed by the direct combination of chlorine and magnesium, and by the action of chlorine on magnesium oxide, oxygen being evolved; this proceeds still more easily **by heating magnesia with charcoal in a stream of chlorine**, when the charcoal serves to take up the oxygen. This latter method is also employed for the preparation of many other chlorides which are formed with still greater difficulty than that of magnesium. Anhydrous magnesium chloride occurs as a colourless, transparent mass, composed of flexible crystalline plates of a pearly lustre. It fuses at a low red heat (708°) into a colourless liquid, remains unchanged in a dry state, but under the action of moisture is partially decomposed even at the ordinary temperature, with formation of hydrochloric acid. When heated in the presence of oxygen (air) it gives chlorine and the basic salt, which is formed with even greater facility under the action of heat in the presence of steam, when HCl is formed, according to the equation: $2\text{MgCl}_2 + \text{H}_2\text{O} = \text{MgO}, \text{MgCl}_2 + 2\text{HCl}$.^{34a}

Calcium (or the metal of lime) and its compounds in many respects present a great resemblance to magnesium compounds, but are also clearly distinguished from them by many properties.³⁵ In general, calcium stands to magnesium in the same relation as potassium does to sodium. Davy obtained metallic calcium, like potassium, as an amalgam, by the action of a galvanic current; but neither

³⁴ According to Thomsen, the combination of MgCl_2 with $6\text{H}_2\text{O}$ evolves 33,000 calories, and its solution in an excess of water, 36,000.

^{34a} Hence MgCl_2 may be employed for the preparation of chlorine and hydrochloric acid (Chaps. X. and XI.). In general, magnesium chloride, which is obtained in large quantities from sea water and Stassfurt carnallite, may find numerous practical uses, for in some respects it acts as a kind of acid.

³⁵ There are many other methods of separating calcium from magnesium besides that mentioned above (note 22). Among them it will be sufficient to mention the behaviour of these bases towards a solution of sugar; hydrated *lime* is exceedingly *soluble in an aqueous solution of sugar*, whilst magnesia is but little soluble. All the lime may be extracted from dolomite by burning it, slaking the mixture of oxides thus obtained, and adding a 10 per cent. solution of sugar. Carbonic anhydride precipitates calcium carbonate from this solution. The addition of sugar (molasses) to the lime used for building purposes powerfully increases the binding power of the mortar, as I have myself found. I have been told that in the East (India, Japan) the addition of sugar to cement has long been practised.

charcoal nor iron decomposes calcium oxide, and even sodium decomposes calcium chloride³⁶ with difficulty. But a galvanic current easily decomposes calcium chloride, and metallic sodium somewhat easily decomposes calcium iodide when heated. As in the case of hydrogen, potassium, and magnesium, the affinity of iodine for calcium is feebler than that of chlorine (and oxygen), and therefore it is not surprising that calcium iodide may be subjected to that decomposition, which the chloride and oxide undergo with difficulty.³⁷ **Metallic calcium** is of a yellow colour, and has a considerable lustre, which it preserves in dry air. Its specific gravity is 1.58. Calcium is distinguished by its great ductility: it melts at a red heat and then burns in the air with a very brilliant flame; the brilliancy is due to the formation of finely divided infusible calcium oxide. Judging from the fact that calcium in burning gives a very large flame, it is probable that this metal is volatile. Calcium decomposes water at the ordinary temperature, although with difficulty, and is oxidised in moist air, but not so rapidly as sodium. In burning, it gives its oxide or **lime**, CaO , a substance which is familiar to everyone, and of which we have already frequently had occasion to speak. This oxide is not met with in nature in a free state, because it is an energetic base which everywhere encounters acid substances, forming salts with them. It is generally combined with silica, or occurs as calcium carbonate or sulphate. The carbonate and nitrate are decomposed, at a red heat, with the formation of lime. As a rule, the carbonate, which is so frequently met with in nature, serves as the source of the calcium oxide, both commercial and pure. When heated, calcium carbonate dissociates: $\text{CaCO}_3 = \text{CaO} + \text{CO}_2$. In practice the decomposition is conducted at a bright red heat, in the presence either of steam or of a current of a foreign gas, the limestone being either in heaps or in special kilns.³⁸

³⁶ Moreover Caron obtained an alloy of calcium and zinc by fusing calcium chloride with zinc and sodium. The zinc distilled from this alloy at a white heat, leaving calcium behind (note 50).

³⁷ Calcium iodide may be prepared by saturating lime with hydriodic acid. It is a very soluble salt (at 20° one part of the salt requires 0.49 part, and at 43° , 0.35 part of water for solution), is deliquescent in the air, and resembles calcium chloride in many respects. If anhydrous calcium iodide is heated with an equivalent quantity of sodium in a closely covered iron crucible, sodium iodide and metallic calcium are formed (Liés-Bodart). In the presence of an excess of sodium it forms an alloy with Ca, and may be separated from it by alcohol. At the temperature of the electric furnace CaO gives Ca with carbon, but it is immediately converted into carbide.

³⁸ Kilns which act either intermittently or continuously are built for this purpose. Those of the first kind are filled with alternate layers of fuel and limestone; the fuel is lighted, and the heat developed by its combustion serves for decomposing the limestone. When the process is completed the kiln is allowed to cool somewhat, the lime raked out, and the same process repeated. In the continuously acting furnaces, constructed like

Calcium oxide—that is, quicklime—is a substance (sp. gr. 3·15) which is unaffected by furnace heat,³⁹ and may therefore serve as a fire-resisting material, and was employed by Deville for the construction of furnaces in which platinum was melted and silver volatilised, by the action of the heat evolved by the combustion of detonating gas; but lime fuses into a mobile liquid at the temperature of the electric furnace (about 3000°), and even volatilises (Moissan), and under these conditions magnesia resists the action of heat even more than lime. The hydrated lime, slaked lime, or calcium hydroxide, CaH_2O_2 (specific gravity 2·07), is a most common alkaline substance, employed largely in building for making mortars or cements, in which case its binding property is mainly due to the absorption of carbonic anhydride.⁴⁰ Lime, like other alkalies,

that shown in fig. 88, the kiln itself only contains limestone, and there are lateral hearths for burning the fuel, the flame of which passes through the limestone and serves for its decomposition. Such furnaces are able to work continuously, because the unburnt limestone may be charged from above and the burnt lime raked out from below. It is not every limestone that is suitable for the preparation of lime, because many contain impurities, principally clay, dolomite, and sand. Such limestones when burnt either fuse partially or give an impure lime, called *poor* lime in distinction from that obtained from purer limestone, which is called *rich* lime. The latter kind is characterised by its disintegrating into a fine powder when treated with water, and is suitable for the majority of uses to which lime is applied, and for which the poor lime is sometimes quite unfit. However, certain kinds of poor lime (as we shall see in Chap. XVIII., note 25) are used in the preparation of hydraulic cements, which solidify into a hard mass under water.

In order to obtain perfectly pure lime it is necessary to take the purest possible materials. In the laboratory, marble or shells are used for this purpose as a pure form of calcium carbonate. They are first burnt in a furnace, then put into a crucible and moistened with a small quantity of water, and finally strongly ignited, by which means a pure lime is obtained. Pure lime may be more rapidly prepared by taking calcium nitrate, CaN_2O_6 , which is easily obtained by dissolving limestone in nitric acid. The solution obtained is boiled with a small quantity of lime in order to precipitate the foreign oxides, which are insoluble in water. The oxides of iron, aluminium, &c. are precipitated by this means. The salt is then crystallised and ignited: $\text{CaN}_2\text{O}_6 = \text{CaO} + 2\text{NO}_2 + \text{O}$.

In the decomposition of calcium carbonate the lime preserves the form of the lumps subjected to ignition; this is one of the signs distinguishing **quicklime** when it is freshly burnt and unaltered by air. It attracts moisture from the air and then disintegrates to a powder; if left long exposed in the air, it also attracts carbonic anhydride and increases in volume; it does not entirely pass into carbonate, but forms a compound of the latter with caustic lime.

³⁹ Lime, when raised to a white heat in the vapour of potassium, gives calcium, and in chlorine it gives off oxygen. Sulphur, phosphorus, &c., when heated with lime, are absorbed by it.

⁴⁰ The greater quantity of lime is used in making mortar for binding bricks or stones together, in the form of **lime** or **cement**, or the so-called **slaked lime**. For this purpose the lime is mixed with water and sand, which serves to separate the particles of lime from each other. If only lime paste were put between two bricks they would not hold firmly together, because after the water had evaporated the lime would occupy a smaller space than before, and therefore cracks and powder would form in its mass, so that it would by no means produce that complete cementation of the bricks which it is desired

acts on many animal and vegetable substances, and for this reason has many practical uses—for example, for removing fats, and in agriculture

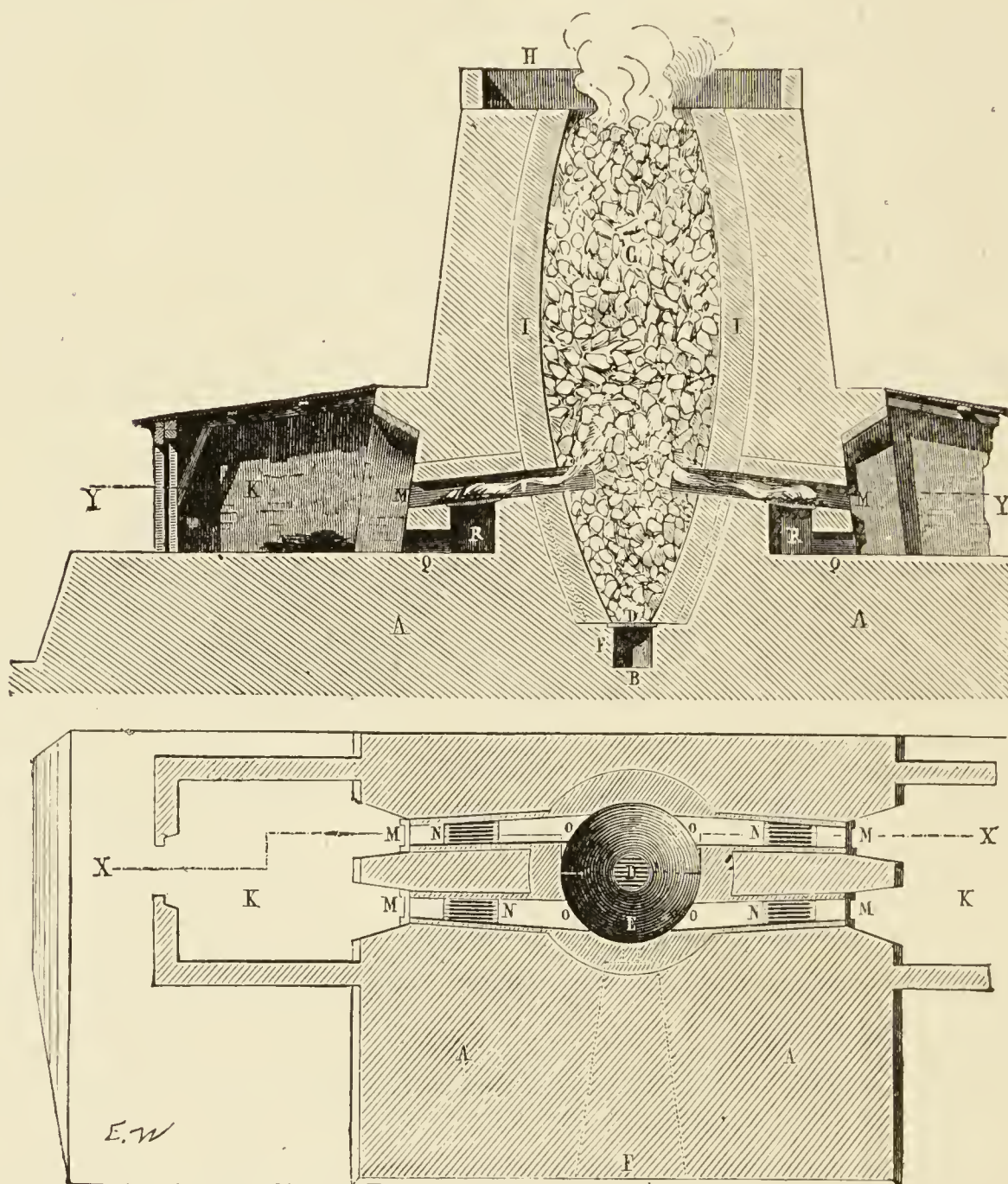


FIG. 88.—Continuously acting kiln for burning lime. The lime is charged from above and calcined by four lateral grates, R, M; D, fire-bars; B, space for withdrawing the burnt lime; K, stoke-house; M, fire-grate; Q, R, under-grate.

for accelerating the decomposition of organic substances in the so-called **composts** or accumulations of vegetable and animal remains used for

to attain. Pieces of stone—that is, sand—mixed with the lime hinder this process of disintegration, because the lime binds together the individual grains of sand mixed with it, and forms one concrete mass, after the desiccation or removal of the water. The process of the solidification of lime, taken as **slaked lime**, consists first in the direct evaporation of the water and crystallisation of the hydrate, so that the lime binds the stones and sand mixed with it, just as glue binds two pieces of wood. But this preliminary binding action of lime is feeble (as is seen by direct experiment) unless there be further alteration of the lime leading to the formation of carbonates, silicates, and other salts of calcium which are distinguished by their great cohesiveness. With the progress of time the cement is partially subjected to the action of the carbonic anhydride in the air, owing to which calcium carbonate is formed, but not more than half the lime is thus

fertilising land. Calcium hydroxide easily loses its water at a moderate heat (530°), but it does not part with water at 100° . When mixed with water, lime forms a pasty mass known as **slaked lime** and in a more dilute form as **milk of lime**, because when shaken up in water it remains suspended in it for a long time and presents the appearance of a milky liquid. But, besides this, lime is directly soluble in water, not to any considerable extent, but still in such quantity that **lime water** is precipitated by carbonic anhydride, and has clearly distinguishable alkaline properties. One part of the lime requires at the ordinary temperature about 800 parts of water for solution. At 100° it requires about 1,500 parts of water, and therefore lime-water becomes cloudy when boiled. If lime-water is evaporated in a vacuum, calcium hydroxide separates in six-sided crystals.⁴¹ If lime-water is mixed with hydrogen peroxide, minute crystals of **calcium peroxide**, $\text{CaO}_2 \cdot 8\text{H}_2\text{O}$, separate; this compound is very unstable, and, like barium peroxide, is decomposed by heat. Lime, as a powerful base, combines with all acids, and in this respect presents a transition from the true alkalies to magnesia. Many of the salts of calcium (the carbonate, phosphate, borate, and oxalate) are insoluble in water; the sulphate is only sparingly soluble. As a more energetic base than magnesia, lime forms salts, CaX_2 , which are distinguished by their stability in comparison with the salts MgX_2 ; lime does not form basic and double salts as easily as magnesia.

Anhydrous lime does not absorb dry carbonic anhydride at the ordinary temperature. This was already known by Scheele, and Prof. Schuliachenko showed that there is no absorption even at 360° . This only proceeds at a red heat,⁴² and then only leads to the formation of a

converted into carbonate. Besides which, the lime acts on the silica of the bricks, and it is owing to these new combinations simultaneously forming in the cement that it gradually becomes stronger and stronger. Hence the binding action of the lime becomes stronger with the lapse of time. This is the reason (and not, as is sometimes said, because the ancients knew how to build stronger than we do) why buildings which have stood for centuries contain a very strongly binding cement. Hydraulic cements will be described later (Chap. XVIII., note 25).

⁴¹ Professor Glinka measured the transparent bright crystals of calcium hydroxide which are formed in common hydraulic (Portland) cement.

⁴² The act of heating brings the substance into that state of internal motion which is required for reaction. It should be considered that by the act of heating, not only is the motion or store of energy of the whole molecule increased, but also, in all probability, the motion of the atoms themselves in the molecules undergoes a change. The same kind of change is accomplished by the act of solution, or of combination in general, judging from the fact that a dissolved or combined substance—for instance, lime with water—reacts on carbonic anhydride as it does under the action of heat. For the comprehension of chemical phenomena it is exceedingly useful to recognise clearly this parallelism. Rose's observation on the formation (by the slow diffusion of solutions of calcium chloride in sodium carbonate) of aragonite from dilute, and of calc spar from strong, solutions is

mixture of calcium oxide and carbonate (Rose). But if the lime be slaked or dissolved, the absorption of carbonic anhydride proceeds rapidly and completely. These phenomena are connected with the **dissociation of calcium carbonate**, studied by Debray (1867) under the influence of the conceptions of dissociation introduced into science by Henri Saint-Claire Deville. After Debray, dissociation was also studied by Le Chatelier. Just as there is no vapour pressure for non-volatile substances, so there is no dissociation pressure of carbonic anhydride for calcium carbonate at the ordinary temperature. Just as every volatile substance has a maximum possible vapour pressure for every temperature, so also calcium carbonate has its corresponding **dissociation pressure**; and the pressure of the gas driven off rises from 0 to 100 mm. of mercury at temperatures of 400° – 700° ; it goes on increasing from 700° to 900° , but (according to Debray) does not equal the atmospheric pressure (760 mm.) even at the boiling-point of zinc (about 930°). Just as, if the pressure be greater, there will be no evaporation, so also there will be no decomposition. Debray took crystals of calc spar, and could not observe the least change in them at the boiling-point of zinc (930°) in an atmosphere of carbonic anhydride taken at the atmospheric pressure (760 mm.), whilst on the other hand calcium carbonate may be completely decomposed at a much lower temperature if the pressure of the carbonic anhydride be kept below the dissociation pressure, which may be done either by directly pumping away the gas with an air-pump or by mixing it with some other gas—that is, by diminishing the partial pressure of the carbonic anhydride,⁴³ just as an object may be dried at the ordinary temperature by removing the aqueous vapour or by carrying it off in a stream of another gas. Thus it is possible to obtain calcium carbonate from lime and carbonic anhydride at a certain temperature above that at which dissociation begins, and conversely to decompose calcium carbonate at the same temperature into lime and carbonic anhydride.⁴⁴ At the ordinary

easily understood from this point of view. As aragonite is always formed from hot solutions, it appears that dilution with water acts like heat.

⁴³ Experience has shown that by moistening partially burnt lime with water and reheating it, it is easy to drive off the last traces of carbonic anhydride from it, and that, in general, by blowing air or steam through the lime, and even by using moist fuel, it is possible to accelerate the decomposition of the calcium carbonate. The partial pressure is decreased by these means.

⁴⁴ Before Deville's time decompositions like that under consideration were understood to start at a certain temperature, and to be accelerated by a rise of temperature, but it was not considered possible that combination could proceed at the same temperature as that at which decomposition goes on. The followers of Deville (Debray, Troost, Lemoine, Hautefeuille, Le Chatelier, and others) gave many data, and among other things have shown the close resemblance between the phenomena of evaporation and dissociation, and pointed out that the amount of heat absorbed by a dissociating sub-

temperature the reaction of the first order (combination) cannot proceed because the second (decomposition, dissociation) cannot take place, and thus all the most important phenomena with respect to the behaviour of lime towards carbonic anhydride are explained by starting from one common basis.⁴⁵

Calcium carbonate, CaCO_3 , is sometimes met with in nature in a crystalline form, and it forms an example of the phenomenon termed **dimorphism**—that is, it appears in two crystalline forms. When it exhibits combinations of forms belonging to the hexagonal system (six-sided prisms, rhombohedra, &c.) it is called **calc spar**. Calc spar has a specific gravity of 2·7, and is further characterised by a distinct cleavage along the plains of the fundamental rhombohedron having an angle of 105° . Perfectly transparent *Iceland spar* presents a clear example of double refraction (for which reason it is frequently employed in physical apparatus). The other form of calcium carbonate occurs in crystals belonging to the rhombic system, and it is then called **aragonite**; its specific gravity is 3·0. If calcium carbonate is artificially produced by slow crystallisation at the ordinary temperature, it appears in the rhombohedral form, but if the crystallisation is aided by heat it then appears as aragonite. It may therefore be supposed that calc spar

stance may be calculated according to the law of the variation of dissociation-pressure, in exactly the same manner as it is possible to calculate the latent heat of the evaporation of water, knowing the variation of the pressure with the temperature, on the basis of the second law of thermodynamics. Thus **one and the same conception** of the mechanical theory of heat **is applicable to dissociation and evaporation**. Details of this subject must be looked for in special works on physical chemistry.

⁴⁵ But the question as to the formation of a basic calcium carbonate with a rise of temperature still remains undecided. The presence of water complicates all the relations between lime and carbonic anhydride, especially as the existence of an attraction between calcium carbonate and water is seen from its being able to give a **crystallohydrate**, $\text{CaCO}_3 \cdot 5\text{H}_2\text{O}$ (Pelouze), which crystallises in rhombic prisms of sp. gr. about 1·77 and loses its water at 20° . These crystals are obtained when a solution of lime in sugar and water is left long exposed to the air and slowly attracts carbonic anhydride from it, and also by the evaporation of such a solution at a temperature of about 3° . On the other hand, it is probable that an **acid salt**, $\text{CaH}_2(\text{CO}_3)_2$, is formed in an aqueous solution, not only because water containing carbonic acid dissolves calcium carbonate, but more especially in view of the researches of Schloesing (1872), which showed that at 16° a litre of water in an atmosphere of carbonic anhydride (pressure 0·984 atmosphere) dissolves 1·086 gram of calcium carbonate and 1·778 gram of carbonic anhydride, which corresponds with the formation of calcium hydrogen carbonate, and the solution of carbonic anhydride in the remaining water. Caro showed that a litre of water is able to dissolve as much as 3 grams of calcium carbonate if the pressure be increased to 4 or more atmospheres. The calcium carbonate is precipitated when the carbonic anhydride passes off in the air or in a current of another gas; this also takes place in many natural springs. Tufa, stalactites, and other like formations from waters containing calcium carbonate and carbonic acid in solution are formed in this manner. The solubility of calcium carbonate itself at the ordinary temperature does not exceed 13 milligrams per litre of water.

presents the form corresponding with a low temperature, and aragonite that with a higher temperature, during crystallisation.⁴⁶

Calcium sulphate in combination with two equivalents of water, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, is very widely distributed in nature, and is known as **gypsum**. Gypsum loses one and a half and two equivalents of water at a moderate temperature,⁴⁷ and anhydrous or burnt gypsum is then obtained, which is also known as plaster of Paris, and is employed in large quantities for modelling.⁴⁸ This use depends on the fact that

⁴⁶ Dimorphous bodies are distinguished from true isomerides and polymerides in that they do not differ in their chemical reactions, which are determined by a difference in the distribution (motion) of the atoms in the molecules, and therefore dimorphism is usually ascribed to a difference in the distribution of the similar molecules, building up the crystals. Although such an hypothesis is quite admissible in the spirit of the atomic and molecular theory, yet, as in another distribution of the molecules, a perfect conservation of the distribution of the atoms in them cannot be imagined, and in every effort of chemical reaction there must take place a certain motion among the atoms; so that, in my opinion, there is no firm basis for distinguishing dimorphism from the general conception of isomerism under which the cases of those organic bodies which are dextro- and lævo-rotatory (with respect to polarised light) have recently been brought with such brilliant success. When calcium carbonate separates out from solutions, it has at first a gelatinous appearance, which leads to the supposition that this salt appears in a colloidal state. It only crystallises with the progress of time. It is probable (Tammann) that solids always appear first in the form of colloids and then acquire a crystalline form with more or less ease. The colloidal state of calcium carbonate is particularly clear from the following observations made by Prof. Famintzin, who showed that when it separates from solutions it is obtained under certain conditions in the form of grains having the peculiar paste-like structure proper to starch, which fact has not only an independent interest, but presents an example of a mineral substance being obtained in a form until then only known in the organic substances elaborated in plants. This shows that the forms (cells, vessels &c.) in which vegetable and animal substances occur in organisms do not present in themselves anything peculiar to organisms, but are only the result of those particular conditions in which these substances are formed. Traube, and afterwards Monnier and Vogt (1882), by means of a similar slow formation of precipitates (by reacting on sulphates of different metals with sodium silicate or carbonate), obtained formations which, under the microscope, were in every respect identical in appearance with vegetable cells.

⁴⁷ According to Le Chatelier (1888), $1\frac{1}{2}\text{H}_2\text{O}$ is lost at 120° , and according to van't Hoff at 107° , that is, $\text{H}_2\text{O} \cdot 2\text{CaSO}_4$ is formed, but at 194° all the water is expelled. According to Shenstone and Cundall (1888) gypsum begins to lose water at 70° in dry air. The hemi-hydrated compound $\text{H}_2\text{O} \cdot 2\text{CaSO}_4$ is also formed when gypsum is heated with water in a closed vessel at 150° (Hoppe-Seyler). It is evident that the transition point between the di- and hemi-hydrated salts lies at about 107° , that is to say, at this temperature we can simultaneously have a solution of CaSO_4 in water (and its vapour), $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$. At higher temperatures, only the latter salt will be present, and at lower temperatures only the di-hydrated salt. This is an example of the doctrine of phases (see Chap. XXIV., note 9, &c.).

⁴⁸ For stucco-work it is usual to add lime and sand, as the mass is then harder and does not solidify so quickly. For imitating marble, glue is added to the plaster, and the mass is polished when thoroughly dry. Re-burnt gypsum cannot be used over again, as that which has once solidified is, like the natural anhydride, not able to recombine with water. It is evident that the structure of the molecules in the crystallised mass, or in general in any dense mass, exerts an influence on the chemical action, which is more particularly evident in metals in their different forms (powder, crystalline, rolled, &c.).

burnt and finely divided and sifted gypsum forms a paste when mixed with water; after a certain time this paste becomes slightly heated and solidifies, owing to the fact that the anhydrous calcium sulphate, CaSO_4 , again combines with water. When the plaster of Paris and water are first made into a paste they form a mechanical mixture, but when the mass solidifies a compound of the calcium sulphate with two molecules of water is then produced; and this may be regarded as derived from S(OH)_6 by the substitution of two atoms of hydrogen by one atom of bivalent calcium. Natural gypsum sometimes appears as perfectly colourless, or variegated, marble-like masses, and sometimes in perfectly colourless crystals, **selenite**, of specific gravity 2.33. The semi-transparent gypsum, or **alabaster**, is often carved into small statues. Besides which an anhydrous calcium sulphate, CaSO_4 , called **anhydrite** (specific gravity 2.97), occurs in nature. It sometimes occurs along with gypsum. It is no longer capable of combining directly with water, and differs in this respect from the anhydrous salt obtained by gently igniting gypsum. If gypsum be very strongly heated it shrinks and loses its power of combining with water.^{48a} One part of calcium sulphate requires at 0° , 525 parts of water for solution; at 38° , 466 parts; and at 100° , 571 parts of water. The maximum solubility of gypsum is at about 36° , which is nearly the same temperature as that at which sodium sulphate is most soluble. The anhydrous salt evolves considerable heat with water.⁴⁹

^{48a} According to MacColeb, gypsum dehydrated at 200° has a specific gravity 2.577, and after being heated to its point of fusion, 2.654. Potilitzin (1894) also admits the two above-named modifications of anhydrous gypsum, which, moreover, always contain the hemi-hydrated hydrate (note 47), and he explains by their relation to water the phenomena observed in the solidification of a mixture of burnt gypsum and water.

⁴⁹ According to G. Halett and L. Allen (1902), 100 cc. of a saturated CaSO_4 solution contains: at 0° , 0.176 gm.; at 10° , 0.193 gm.; at 25° , 0.208 gm.; at 30° , 0.209 gm.; at 36° , 0.2096 gm.; at 40° , 0.2097 gm.; at 45° , 0.208 gm.; and at 100° , 0.162 gm. Thus the greatest solubility corresponds to about 40° . As Marignac showed, gypsum, especially when desiccated at 120° , readily gives supersaturated solutions with respect to $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, which contain as much as 1 part of CaSO_4 to 110 parts of water. Boiling dilute hydrochloric acid dissolves gypsum, forming calcium chloride. The behaviour of gypsum towards the alkaline carbonates has been described in Chapter X. Alcohol precipitates gypsum from its aqueous solutions, because, like the sulphates in general, gypsum is sparingly soluble in alcohol. Gypsum, like all the sulphates, when heated with charcoal, gives up its oxygen, forming the sulphide, CaS .

Like magnesium sulphate, calcium sulphate is capable of forming double salts, but only with difficulty, and these compounds are chemically less stable than the corresponding magnesium ones. They contain, as is always the case with double salts, less water of crystallisation than the component salts. Rose, Struvé, and others obtained the salt $\text{CaK}_2(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$; a mixture of gypsum with an equivalent amount of potassium sulphate and water solidifies into a homogeneous mass. Fritzsche obtained the corresponding sodium salt in the hydrated and anhydrous states, by heating a mixture of gypsum with a saturated solution of sodium sulphate. The anhydrous salt occurs in

As lime is a more energetic base than magnesia, so **calcium chloride**, CaCl_2 , is not so easily decomposed by water as magnesium chloride, and its solutions only disengage a small quantity of hydrochloric acid when evaporated, and when the evaporation is conducted in a stream of hydrochloric acid it easily gives an anhydrous salt which fuses at 719° ; otherwise an aqueous solution yields a crystallo-hydrate, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, which melts at 30° .⁵⁰

nature as *glauberite*. Fritzsche also obtained *gaylussite*, $\text{Na}_2\text{Ca}(\text{CO}_3)_2 \cdot 5\text{H}_2\text{O}$, by pouring a saturated solution of sodium carbonate on to freshly precipitated calcium carbonate. Calcium also forms basic salts, but only in small number. Veeren (1892) obtained $\text{Ca}(\text{NO}_3)_2 \cdot \text{Ca}(\text{OH})_2 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ by leaving powdered caustic lime in a saturated solution of $\text{Ca}(\text{NO}_3)_2$ until it solidified. This salt is decomposed by water.

⁵⁰ Calcium chloride has a specific gravity 2.20, or, when fused, 2.12, and the sp. gr. of the crystallised salt $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ is 1.69. If the volume of the crystals at 0° is taken as 1, then at 29° it is 1.020, and the volume of the fused mass at the same temperature is 1.118 (Kopp) (specific gravity of solutions, see note 27). The solution containing 50 per cent. of CaCl_2 boils at 130° , and that with 70 per cent. at 158° . Calcium chloride is soluble in alcohol and absorbs ammonia.

A gram molecular weight of calcium chloride in dissolving in an excess of water evolves 18,723 calories, and in dissolving in alcohol 17,555 units of heat (according to Pickering).

Bakhuis Roozeboom made detailed researches on the crystallo-hydrates of calcium chloride (1889), and found that $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ melts at 30.2° , and is formed at low temperatures from solutions containing not more than 103 parts of calcium chloride per 100 parts of water; if the amount of salt (always to 100 parts of water) reaches 120 parts, then tabular crystals of $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}\beta$ are formed, which at temperatures above 38.4° are converted into the crystallo-hydrates $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, whilst at temperatures below 18° the β variety passes into the more stable $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}\alpha$, which process is aided by mechanical friction. Hence, as is the case with magnesium sulphate (note 27), one and the same crystallo-hydrate appears in two forms—the β , which is easily produced but unstable, and the α , which is stable. The solubility of the above-mentioned hydrates of chloride of calcium, or the amount of calcium chloride per 100 parts of water, is as follows:—

	0°	20°	30°	40°	60°
$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$	60	75	100	—	—
$\text{CaCl}_2 \cdot 4\text{H}_2\text{O}\alpha$	—	90	101	117	—
$\text{CaCl}_2 \cdot 4\text{H}_2\text{O}\beta$	—	104	114	—	—
$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$	—	—	—	128	137

The point of intersection of the curves of solubility lies at about 30° for the first two salts and at about 45° for the salts with $4\text{H}_2\text{O}$ and $2\text{H}_2\text{O}$. The crystals $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ may, however, be obtained (Ditte) at the ordinary temperature from solutions containing hydrochloric acid. The vapour pressure of this crystallo-hydrate equals the atmospheric pressure at 165° , and therefore the crystals may be dried in an atmosphere of steam and obtained without a mother liquor, the vapour pressure of which is greater. This crystallo-hydrate decomposes at about 175° into $\text{CaCl}_2 \cdot \text{H}_2\text{O}$ and a solution; this is easily brought about in a closed vessel when the pressure is greater than that of the atmosphere. This crystallo-hydrate is destroyed at temperatures above 260° , anhydrous calcium chloride being formed.

Neglecting the unstable modification, $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}\beta$, we will give the temperatures t at which the passage of one hydrate into another takes place and at which the solution, $\text{CaCl}_2 + n\text{H}_2\text{O}$, the two solids A and B and aqueous vapour, whose pressure, p , is given

Just as for potassium, $K=39$ (and sodium, $Na=23$), there are the near analogues, $Rb=85$ and $Cs=133$, and also another, $Li=7$, so in exactly the same manner, for calcium $Ca=40$ (and magnesium, $Mg=24$), there is another analogue of lower atomic weight, beryllium, $Be=9$, besides the near analogues strontium, $Sr=87$, and barium, $Ba=137$. As rubidium and caesium are more rarely met with in nature than potassium, so also strontium and barium are rarer than calcium (just as bromine and iodine are rarer than chlorine). Since they exhibit many points of resemblance with calcium, strontium and barium may be characterised after a very short acquaintance with their chief compounds; this shows the important advantages gained by distributing the elements according to their natural groups, to which matter we shall turn our attention in the next chapter.

Among the compounds of barium met with in nature the commonest is the **sulphate**, $BaSO_4$, which forms anhydrous crystals of the rhombic system, which are identical in their crystalline form with anhydrite, and generally occur as transparent and semi-transparent masses of tabular crystals having a high specific gravity, namely, 4.45, for which reason this salt bears the name of **heavy spar** or **barytes**. Analogous to it is **celestine**, $SrSO_4$, which is, however, more rarely met with. Heavy spar frequently forms the gangue separated on dressing metallic ores from the vein material; this mineral is the source of all other barium compounds; for the carbonate, although more easily transformed into the other compounds (because acid acts directly on it, evolving carbonic anhydride), is a comparatively rare mineral ($BaCO_3$ forms the mineral *witherrite*; $SrCO_3$, *strontianite*; both are rare, the latter being found at Etna). The treatment of barium sulphate is rendered difficult from the fact that it is insoluble both in water and

in millimetres, are able to exist together in stable equilibrium, according to Roozeboom's determinations:

t	n	A	B	p
-55°	14.5	ice	$CaCl_2, 6H_2O$	0
$+29.8^\circ$	6.1	$CaCl_2, 6H_2O$	$CaCl_2, 4H_2O$	6.8
45.3°	4.7	$CaCl_2, 4H_2O$	$CaCl_2, 2H_2O$	11.8
175.5°	2.1	$CaCl_2, 2H_2O$	$CaCl_2, H_2O$	842
260°	1.8	$CaCl_2, H_2O$	$CaCl_2$	Several atmospheres

Solutions of calcium chloride may serve as a convenient example for the study of supersaturation, which in this case easily occurs, because different hydrates are formed. Thus at 25° , solutions containing more than 83 parts of anhydrous calcium chloride per 100 of water will be supersaturated for the hydrate $CaCl_2, 6H_2O$.

Hammerl showed that solutions of calcium chloride, when frozen, deposit ice if they contain less than 43 parts of salt per 100 of water, and if more, the crystallo-hydrate, $CaCl_2, 6H_2O$, separates, and that a solution of the above composition ($CaCl_2, 14H_2O$, requiring 44.0 parts calcium chloride per 100 of water) solidifies as a cryo-hydrate at about -55° .

acids, and has therefore to be treated by a method of reduction.⁵¹ Like sodium sulphate and calcium sulphate, heavy spar when heated with charcoal parts with its oxygen and forms barium sulphide, BaS. For this purpose a pasty mixture of powdered heavy spar, charcoal, and tar is subjected to the action of a strong heat, when $\text{BaSO}_4 + 4\text{C} = \text{BaS} + 4\text{CO}$. The residue is then treated with water, in which the barium sulphide is soluble.⁵² When boiled with hydrochloric acid barium chloride, BaCl_2 , is obtained in solution, and the sulphur is disengaged as gaseous hydrogen sulphide, $\text{BaS} + 2\text{HCl} = \text{BaCl}_2 + \text{H}_2\text{S}$. In this manner barium sulphate is converted into barium chloride,⁵³

⁵¹ The action of barium sulphate on sodium and potassium carbonates is given on p. 459.

⁵² Barium sulphide is decomposed by water, $\text{BaS} + 2\text{H}_2\text{O} = \text{H}_2\text{S} + \text{Ba}(\text{OH})_2$ (the reaction is reversible), but both substances are soluble in water, and their separation is complicated by the fact that barium sulphide absorbs oxygen and gives insoluble barium sulphate. The hydrogen sulphide is sometimes removed from the solution by boiling with the oxide of copper or zinc. If sugar be added to a solution of barium sulphide, barium saccharate is precipitated on heating; it is decomposed by carbonic anhydride, so that barium carbonate is formed. An equivalent mixture of sodium sulphate with barium or strontium sulphate, when ignited with charcoal, gives a mixture of sodium sulphide and barium or strontium sulphide; and if this mixture be dissolved in water and the solution evaporated, barium or strontium hydroxide crystallises out on cooling, and sodium hydrosulphide, NaHS, is obtained in solution. The hydroxides BaH_2O_2 and SrH_2O_2 are prepared on a large scale, being applied to many reactions; for example, strontium hydroxide is prepared for sugar works for extracting crystallisable sugar from molasses.

Boussingault, by igniting barium sulphate in hydrochloric acid gas, obtained a complete decomposition, with the formation of barium chloride. Attention should also be turned to the fact that Grouven, by heating a mixture of charcoal and strontium sulphate with magnesium and potassium sulphates, showed the easy decomposability, depending on the formation of double salts, such as $\text{SrS}, \text{K}_2\text{S}$, which are readily soluble in water and give a precipitate of strontium carbonate with carbonic anhydride. In such examples as these we see that the force which binds double salts may play a part in directing the course of reactions, and the number of double salts of silica on the earth's surface shows that nature takes advantage of these forces in her chemical processes. It is worthy of remark that Buchner (1893), by mixing a 40 per cent. solution of barium acetate with a 60 per cent. solution of sulphate of alumina, obtained a thick glutinous mass, which only gave a precipitate of BaSO_4 after being diluted with water.

⁵³ Barium sulphate is sometimes converted into barium chloride in the following manner: finely ground barium sulphate is heated with coal and manganese chloride (the residue from the manufacture of chlorine). The mass becomes semi-liquid, and when it evolves carbonic oxide the heating is stopped. The following double decompositions proceed during this operation: first the carbon takes up the oxygen from the barium sulphate, and gives sulphide, BaS, which enters into double decomposition with the chloride of manganese, MnCl_2 , forming manganese sulphide, MnS , which is insoluble in water, and soluble barium chloride. This solution is easily obtained pure because many foreign impurities, such as iron, remain in the insoluble portion with the manganese. The solution of barium chloride is chiefly used for the preparation of barium sulphate, which is precipitated by sulphuric acid, by which means **barium sulphate** is re-formed as a powder. This salt is characterised by the fact that it is unacted on by the majority of chemical reagents, is insoluble in water, and is not dissolved by acids. Owing to this, artificial barium sulphate forms a permanent white paint which is used

and the latter by double decomposition with strong nitric acid or nitre gives the less soluble barium nitrate, $\text{Ba}(\text{NO}_3)_2$,⁵⁴ or with sodium carbonate, a precipitate of barium carbonate, BaCO_3 . Both these salts are able to give **barium oxide**, or **baryta**, BaO , and the hydroxide, $\text{Ba}(\text{HO})_2$, which differs from lime by its great solubility in water,⁵⁵ and by the ease with which it forms a crystallo-hydrate, $\text{BaH}_2\text{O}_2, 8\text{H}_2\text{O}$, from its solutions. Owing to its solubility, baryta is frequently employed in manufactures and in practical chemistry, as an alkali which has the very important property that it may be always entirely removed from solution as the insoluble barium sulphate, BaSO_4 , by the addition of sulphuric acid. It may also be removed while it remains in an alkaline state (for example, the excess which may remain when it is used for saturating acids) by means of carbonic anhydride, which also completely precipitates baryta as a sparingly soluble, colourless, and powdery carbonate. Both these reactions show that baryta has such properties as would very greatly extend its use were its compounds as instead of (and mixed with) white lead, and has been termed *blanc fixé*, or 'permanent white.'

The solution of one part of calcium chloride at 20° requires 1.33 part of water, that of one part of strontium chloride, 1.88 part of water at the same temperature, and that of barium chloride, 2.88 parts of water. The solubilities of the bromides and iodides vary in the same proportions. The chlorides of barium and strontium crystallise out from solution with great ease, in combination with water; they form $\text{BaCl}_2, 2\text{H}_2\text{O}$ and $\text{SrCl}_2, 6\text{H}_2\text{O}$. The latter (which separates out at 40°) resembles the salts of Ca and Mg in composition, and Étard (1892) obtained $\text{SrCl}_2, 2\text{H}_2\text{O}$ from solutions at 90° – 130° . We may also observe that the crystallo-hydrates $\text{BaBr}_2, \text{H}_2\text{O}$ and $\text{BaI}_2, 7\text{H}_2\text{O}$ are known (see note 50).

⁵⁴ The nitrates $\text{Sr}(\text{NO}_3)_2$ (in the cold its solutions give a crystallo-hydrate containing $4\text{H}_2\text{O}$) and $\text{Ba}(\text{NO}_3)_2$ are so very sparingly soluble in water that they separate in considerable quantities when a solution of sodium nitrate is added to a strong solution of either barium or strontium chloride. They are obtained by the action of nitric acid on the carbonates or oxides. A hundred parts of water at 15° dissolve 6.5 parts of strontium nitrate and 8.2 parts of barium nitrate, whilst more than 300 parts of calcium nitrate are soluble at the same temperature. Strontium nitrate communicates a crimson coloration to the flame of burning substances, and is therefore frequently used in Bengal fire fireworks and signal lights, for which purpose, however, the salts of lithium are still better fitted. Calcium nitrate is exceedingly hygroscopic. Barium nitrate, on the contrary, does not show this property in the least degree, and in this respect resembles potassium nitrate and is therefore used instead of the latter for the preparation of a gunpowder which is called 'saxifragin powder' (76 parts of barium nitrate, 2 parts of nitre, and 22 parts of charcoal).

⁵⁵ The dissociation of the crystallo-hydrate of baryta is given in Chapter I., note 65. A hundred parts of water dissolve at:

	0°	20°	40°	60°	80°
BaO	1.5	3.5	7.4	18.8	90.8
SrO	0.3	0.7	1.4	3	9

Supersaturated solutions are easily formed.

The anhydrous oxide BaO fuses in the oxyhydrogen flame. When ignited in the vapour of potassium, the latter takes up the oxygen; whilst in chlorine, oxygen is separated and barium chloride formed.

widely distributed as those of sodium and calcium, and were its soluble compounds non-poisonous. Barium nitrate is directly decomposed by the action of heat, barium oxide, BaO , being left behind. The same takes place with barium carbonate, especially that form of it precipitated from solutions, and when mixed with charcoal or ignited in an atmosphere of steam. Barium oxide combines with water with the development of a large amount of heat, and the resultant hydroxide is very stable in its retention of the water, although it parts with it when strongly ignited.^{55a} With oxygen the anhydrous oxide gives, as already mentioned in Chapters III. and IV., a **peroxide**, BaO_2 .⁵⁶ Neither calcium nor strontium oxide is able to give such a peroxide directly and with such facility, but they form peroxides under the action of hydrogen peroxide.

Barium oxide is decomposed when heated in the vapour of potassium; fused barium chloride is decomposed, as Davy showed, by the action of a galvanic current, forming metallic **barium**; and Crookes (1862) obtained an amalgam of barium from which the mercury could easily be driven off,^{56a} by heating sodium amalgam in a saturated solution of barium chloride. Strontium is obtained by the same processes. Both metals are soluble in mercury, and are very slightly volatile. They are both heavier than water, the specific gravity of barium being 3.6, and that of strontium 2.5. Like the metals of the alkalis, they both decompose water at the ordinary temperature.

Barium and strontium as saline elements are characterised by their powerful basic properties, so that they form acid salts with difficulty, and scarcely form basic salts. On comparing them with each other

^{55a} Brugellmann, by heating BaH_2O_2 in a graphite or clay crucible, obtained BaO in needles of sp. gr. 5.32, and by heating in a platinum crucible, in crystals belonging to the cubical system, sp. gr. 5.74. SrO is obtained in the latter form from the nitrate. The following are the specific gravities of the oxides from different sources:—

	MgO	CaO	SrO
from RN_2O_6	3.38	3.25	4.75
„ RCO_3	3.48	3.26	4.45
„ RH_2O_2	3.41	3.25	4.57

⁵⁶ The property of barium oxide of absorbing oxygen when heated, and giving the peroxide, BaO_2 , is very characteristic for this oxide (see Chap. III., note 7). It is only exhibited by the anhydrous oxide. The hydroxide does not absorb oxygen. Barium peroxide is insoluble in water, but is able to form a hydrate with it, and also to combine with hydrogen peroxide, forming a very unstable compound having the composition BaH_2O_4 (obtained by Prof. Schöne), which in course of time evolves oxygen (Chap. IV., note 21).

^{56a} Guntz obtained an amalgam, containing 3 per cent. of barium, by the action of an electric current on a strong solution of BaCl_2 (the mercury was employed as cathode), and he then heated this amalgam at 1000° by means of an electric current, the whole of the mercury being evaporated. The colour of pure barium recalls that of silver. Ba, Sr, and Ca absorb nitrogen, forming N_2R_3 (Maquenne, Moissan).

and with calcium, it is evident that the alkaline properties in this group (as in the group potassium, rubidium, cæsium) increase with the atomic weight, and this succession clearly shows itself in many of their corresponding compounds. Thus, for instance, the solubility of the hydroxides, RH_2O_2 , and the specific gravity⁵⁷ rise in passing from calcium to strontium and barium, while the solubility of the sulphates decreases,⁵⁸ and therefore in the case of magnesium and beryllium, as metals whose atomic weights are still less, we should expect the solubility of the sulphates to be greater, and this is in reality the case.

Just as in the series of the alkali metals we saw the metals potassium, rubidium, and cæsium closely approaching one another in their properties, and allied to them two metals having smaller combining weights—namely, sodium, and the lightest of all, lithium, which all exhibited certain peculiar characteristic properties—so also in the case of the metals of the alkaline earths we find, besides calcium, barium, and strontium, the metal magnesium and also **beryllium** or **glucinum**. In respect to the magnitude of its atomic weight, this last occupies the same position in the series of the metals of the alkaline earths as lithium does in the series of the alkali metals, for the combining weight of beryllium, Be or Gl, is 9. This combining weight is greater than that of lithium (7), just as the combining weight of magnesium (24) is greater than that of sodium (23), and that of calcium (40) greater than that of potassium (39), &c.⁵⁹ Beryllium was so named because it occurs

⁵⁷ Even in solutions a gradual progression in the increase of the specific gravity shows itself, not only for equivalent solutions (for instance, $\text{RCl}_2 + 200\text{H}_2\text{O}$), but even with equal percentage composition, as is seen from the curves giving the specific gravity (water $4^\circ = 10,000$) at 15° (for barium chloride, according to Burdakoff's determinations):

$$\text{BeCl}_2 : S = 9,992 + 67.21p + 0.111p^2$$

$$\text{CaCl}_2 : S = 9,992 + 80.24p + 0.476p^2$$

$$\text{SrCl}_2 : S = 9,992 + 85.57p + 0.733p^2$$

$$\text{BaCl}_2 : S = 9,992 + 86.56p + 0.813p^2$$

⁵⁸ One part of calcium sulphate at the ordinary temperature requires about 500 parts of water for its solution, strontium sulphate about 7,000 parts, barium sulphate about 400,000 parts, whilst beryllium sulphate is readily soluble in water.

⁵⁹ We refer beryllium to the class of the bivalent metals of the alkaline earths—that is, we ascribe to its oxide the formula BeO , and do not consider it as trivalent ($\text{Be} = 13.5$, Chap. VII., note 21), although that view has been upheld by many chemists. The true atomic composition of beryllium oxide was first given by the Russian chemist **Avdéeff** (1819) in his researches on the compounds of this metal. He compared the compounds of beryllium to those of magnesium, and refuted the notion, prevalent at the time, of the resemblance between the oxides of beryllium and aluminium by proving that beryllium sulphate presents a greater resemblance to magnesium sulphate than to aluminium sulphate. It was especially noticed that the analogues of alumina give alums, whilst beryllium oxide, although it is a feeble base, readily giving, like magnesia, basic and double salts, does not form true alums. The establishment of the periodic system of the elements (1869), considered in the following chapter, indicated immediately that

in the mineral **beryl**. The metal is also called **glucinum** (from the Greek word $\gamma\lambda\upsilon\kappa\acute{\upsilon}\varsigma$, sweet), because its salts have a sweet taste. It occurs in beryl, aquamarine, the emerald, and other minerals, which are generally of a green colour; they are sometimes found in considerable masses, but as a rule are comparatively rare and, as transparent crystals, form precious stones. The composition of beryl and of the emerald is as follows: $\text{Al}_2\text{O}_3, 3\text{BeO}, 6\text{SiO}_2$. The Siberian and Brazilian beryls are the best known. The specific gravity of beryl is about 2.7. Beryllium oxide, from the feebleness of its basic properties, presents an analogy to aluminum oxide in the same way that lithium oxide does to magnesium oxide.⁶⁰ Owing to its rare occurrence in nature, to the absence of any especially distinct individual properties, and to the possibility of foretelling them to a certain extent on the basis of the

Avdéeff's view corresponded with the truth—that is, that beryllium is bivalent—and therefore necessitated the denial of its trivalency. This scientific controversy resulted in a long series of researches (1870–80) concerning this element, and ended when Prof. Brauner showed that the chief chemical and physical properties of beryllium and its compounds form a periodic function of the atomic weight, $\text{Be} = 9.1$, and not $\text{Be} = 13.6$, and more especially when Nilson and Pettersson, two of the chief advocates of the trivalency of beryllium, subsequently determined the vapour density of BeCl_2 ($= 40$, Chap. VII., note 21), which gave an undoubted proof of its bivalency (see also note 3). In proclaiming this result Nilson and Pettersson proved that in science truth is equally dear to all, although it may have first been denied by those who afterwards established it (see also note 3).

⁶⁰ Beryllium oxide, like aluminium oxide, is precipitated from solutions of its salts by alkalis, as a gelatinous hydroxide, BeH_2O_2 , which, like alumina, is soluble in an excess of caustic potash or soda. This reaction may be taken advantage of for distinguishing and separating beryllium from aluminium, because when the alkaline solution is diluted with water and boiled, beryllium hydroxide is precipitated, whilst the alumina remains in solution. The solubility of the beryllium oxide at once clearly indicates its feeble basic properties, and, as it were, separates this oxide from the class of the alkaline earths. But on arranging the oxides of the above-described metals of the alkaline earths according to their decreasing atomic weights we have the series:



in which the basic properties and solubility of the oxides consecutively and distinctly decrease until we reach a point when, had we not known of the existence of the beryllium oxide, we should expect to find in its place an oxide insoluble in water and of feeble basic properties. If an alcoholic solution of caustic potash is saturated with the hydrate of BeO , and evaporated under the receiver of an air pump, it forms silky crystals, BeK_2O_2 .

Another characteristic of the salts of beryllium is that they give with aqueous ammonia a gelatinous precipitate which is soluble, like the precipitate of magnesia, in an excess of ammonium carbonate; in this beryllium oxide differs from the oxide of aluminium. Beryllium oxide easily forms a carbonate which is insoluble in water, and resembles magnesium carbonate in many respects. Beryllium sulphate is distinguished by its considerable solubility in water—thus, at the ordinary temperature, it dissolves in an equal weight of water; it crystallises out from its solutions in well-formed crystals, which do not change in the air, and have the composition $\text{BeSO}_4, 4\text{H}_2\text{O}$. When ignited it leaves beryllium oxide, but this oxide, after prolonged ignition, is redissolved by sulphuric acid, whilst aluminium sulphate, after a similar treatment, leaves aluminium oxide, which is no longer soluble in acids. With a few exceptions, the salts of beryllium crystallise with difficulty, and to a considerable extent resemble the salts of magnesium.

periodic system of the elements given in the following chapter, and owing, further, to the brevity of this treatise, we will not discuss at any length the compounds of beryllium, and will only observe that their individuality was pointed out in 1798 by Vauquelin, and that metallic beryllium was obtained by Wöhler and Bussy. Wöhler obtained **metallic beryllium** (like magnesium) by acting on beryllium chloride, BeCl_2 , with potassium (it is best prepared by fusing K_2BeF_4 with Na). Lebeau (1898) obtained Be by the action of an electric current on molten Na_2BeF_4 (BeCl_2 and BF_3 do not conduct an electric current). Metallic beryllium has a specific gravity 1.64 (Nilson and Pettersson). It is very infusible, melting at nearly the same temperature as silver, which it resembles in its white colour and lustre. It is characterised by the fact that it is very difficultly oxidised, and even in the oxidising flame of the blowpipe is only superficially covered with a coating of oxide; it does not burn in pure oxygen, and does not decompose water at the ordinary temperature or at a red heat, but gaseous hydrochloric acid is decomposed by it when slightly heated, with evolution of hydrogen and development of a considerable amount of heat. Even dilute hydrochloric acid acts in the same manner at the ordinary temperature. Beryllium also acts readily on sulphuric acid, but it is remarkable that neither dilute nor strong nitric acid acts on beryllium, which seems especially able to resist oxidising agents. Potassium hydroxide acts on beryllium as on aluminium, hydrogen being disengaged and the metal dissolved, but ammonia has no action on it. These properties of metallic beryllium seem to isolate it from the series of the other metals described in this chapter; but if we compare the properties of calcium, magnesium, and beryllium, we shall see that magnesium occupies a position intermediate between Ca and Be. Whilst calcium decomposes water with great ease, magnesium does so with difficulty, and beryllium not at all. The peculiarities of beryllium among the metals of the alkaline earths recall the fact that in the series of the halogens we saw that fluorine differed from the other halogens in many of its properties and had the smallest atomic weight. The same is the case with regard to beryllium among the other metals of the alkaline earths.

In concluding the characteristics of the compounds of the metals of the alkaline earths, we must add that, like the alkali metals, they combine with nitrogen and hydrogen, and while sodium nitride (obtained by igniting the amide of sodium, Chap. XII., note 44a) and lithium nitride (obtained by heating lithium in nitrogen, Chap. XIII., note 39) have the composition R_3N , so the nitrides of magnesium (note 14), calcium, strontium, and barium have the composition R_3N_2 ,

for example, Ba_3N_2 , as might be expected from the diatomicity of the metals of the alkaline earths and from the relation of the nitrides to ammonia, which is obtained from all of these compounds by the action of water. The **nitrides** of Ca, Sr, and Ba are formed directly (Maquenne, 1892) by heating the metals in nitrogen. They all have the appearance of an amorphous dark-coloured powder; as regards their reactions, it is known that, besides disengaging ammonia with water, they form cyanides when heated with carbonic oxide, for instance: $\text{Ba}_3\text{N}_2 + 2\text{CO} = \text{Ba}(\text{CN})_2 + 2\text{BaO}$.⁶¹

The metals of the alkaline earths, like Na and K, absorb gaseous hydrogen, and form easily oxidisable metallic hydrides. The **hydrides of the metals of the alkaline earths** were discovered by C. Winkler (1891) in investigating the reducibility of these metals by magnesium, but Moissan studied this subject more closely, and showed that crystalline calcium absorbs hydrogen with avidity and even bursts into a flame when heated in a stream of the gas, forming a colourless crystalline hydride, CaH_2 (sp. gr. 1.7) which does not decompose at 600° , and gives hydrogen and lime under the action of water: $\text{CaH}_2 + \text{H}_2\text{O} = \text{CaO} + 2\text{H}_2$.

The metals of the alkaline earths also form compounds with carbon (**carbides**), having the composition C_2M , corresponding to acetylene, C_2H_2 , and indeed easily and directly form this gas under the action of water: $\text{C}_2\text{Ca} + \text{H}_2\text{O} = \text{CaO} + \text{C}_2\text{H}_2$. They were first obtained by Maquenne (1892) by heating a 20 per cent. amalgam of the metal of the alkaline earth with carbon in a stream of hydrogen or by heating the oxide (or even carbonate) with magnesium and carbon (for instance: $\text{BaCO}_3 + 3\text{Mg} + \text{C} = 3\text{MgO} + \text{BaC}_2$). Moissan obtained the same carbides by heating the oxides with carbon in the electric furnace. The most important of these substances from an industrial point of view is the **carbide of calcium**, C_2Ca , which is used for the preparation of acetylene (in lamps for lighting) for enriching lighting gas and as a reducing agent. It is everywhere prepared on a large scale by the action of carbon on lime in the electric furnace: $\text{CaO} + 3\text{C} = \text{C}_2\text{Ca} + \text{CO}$. The current used is several thousand ampères at about 55 volts, and is often generated by water power. Perfectly pure C_2Ca is colourless, resembling common salt, and has the sp. gr. 2.3; but the commercial product contains many impurities, and is brown and almost opaque.⁶² Be, Mg, Sr, and Ba give similar carbides, C_2M , evolving acetylene with water.

⁶¹ Thus in the nitrides of the metals we have substances by means of which we can easily obtain from the nitrogen of the air, not only ammonia, but also with the aid of CO, by synthesis, a whole series of complex carbon and nitrogen compounds.

⁶² Moissan (1897) also obtained C_2Ca and similar carbides by means of those

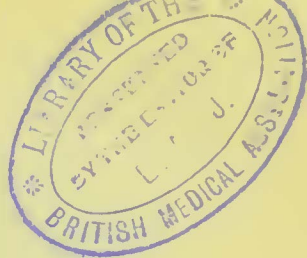
Thus the analogies and correlation of the metals of this group are now clearly marked, not only in their behaviour towards oxygen, chlorine, acids, &c., but also in their capability of combining with nitrogen, hydrogen, and carbon, which latter fact has become known comparatively lately.

compounds of ammonia with the metals which are mentioned in Chap. IV., note 14; his method is as follows: If acetylene acts upon the liquid ammonia compound of the metal (assuming it to be monatomic like Na) NH_3M (at a low temperature, when these compounds are stable), it gives a colourless liquid of the composition C_2HM (according to the equation: $2\text{NH}_3\text{M} + 3\text{C}_2\text{H}_2 = 2\text{C}_2\text{HN} + 2\text{NH}_3 + \text{C}_2\text{H}_4$), that is to say, it forms ethylene; the resultant liquid, on heating, forms C_2M_2 according to the equation: $2\text{C}_2\text{HN} = \text{C}_2\text{H}_2 + \text{C}_2\text{M}_2$, which proves its direct relation to acetylene. When heated with carbon, CaH_2 and Ca_3N_2 give colourless CaC_2 .

END OF THE FIRST VOLUME.

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CHAPTER XV

THE GROUPING OF THE ELEMENTS AND THE PERIODIC LAW

It is seen from the examples given in the preceding chapters that the analogies existing among the elements may be many-sided and more or less complete. Thus lithium and barium are in some respects analogous to sodium and potassium, and in others to magnesium and calcium. It is evident, therefore, that for a true judgment it is necessary to have, not only qualitative, but also quantitative and measurable data. When a property can be measured it ceases to be arbitrary, and renders the comparison objective.

Among these measurable properties of the elements and their corresponding compounds are: (*a*) isomorphism, or the analogy of crystalline forms; and, connected with it, the power to form crystalline mixtures which are isomorphous; (*b*) the relations between the volumes of analogous compounds of the elements; (*c*) the composition of their saline compounds; and (*d*) the relations of the atomic weights of the elements. In this chapter we shall briefly consider these four aspects of the matter, which are exceedingly important for a natural and fruitful grouping of the elements, facilitating, not only a general acquaintance with them, but also their detailed study.

Historically the first, and an important and convincing, method for finding a relationship between the compounds of two different elements is by means of **isomorphism**. This conception was introduced into chemistry by **Mitscherlich** (in 1820), who demonstrated that the corresponding salts of arsenic acid, H_3AsO_4 , and phosphoric acid, H_3PO_4 , crystallise with equal proportions of water, exhibit an exceedingly close resemblance in their crystalline form (as regards the angles of their faces and axes), and are able to crystallise together from solutions, forming crystals containing a mixture of these compounds. Isomorphous

substances are those which, with the same number of atoms in their molecules, present analogous chemical reactions, a close resemblance in their properties, and a similar or very nearly similar crystalline form: they often contain certain elements in common, from which it is to be concluded that the remaining elements (as in the preceding example of As and P) are analogous to each other. And inasmuch as crystalline forms are capable of exact measurement, the external form is evidently as great a help in judging of the internal forces acting between the atoms as is a comparison of reactions, vapour densities, and other similar relations. We have already seen examples of this in the preceding pages.¹ It will be sufficient to call to mind that the compounds of the alkali metals with the halogens, RX , in a crystalline form, all belong to the cubic system and crystallise in octahedra or cubes—for example, sodium chloride, potassium iodide, rubidium chloride, &c. The nitrates of rubidium and caesium appear in anhydrous crystals of the same form as potassium nitrate. The carbonates of the metals of the alkaline earths are isomorphous with calcium carbonate—that is, they appear either in forms like calc spar or in crystals of the rhombic system analogous to aragonite.^{1a} Furthermore, sodium nitrate crystallises in rhombohedra, closely resembling the rhombohedra of calc spar (calcium carbonate), $CaCO_3$, whilst potassium nitrate appears in the same form as aragonite, $CaCO_3$, and the number of atoms in both kinds of salts is the same: they all contain one atom of a metal (K, Na, Ca), one atom of a non-metal (C, N), and three atoms of oxygen. The analogy of form evidently coincides with analogy of atomic composition. But the description of these salts shows that there is no close resemblance in their properties. It is evident that calcium carbonate approaches more nearly to magnesium carbonate than to sodium nitrate, although their crystalline forms are all very nearly the same. Isomorphous substances which are perfectly analogous to each other are characterised not only by a close resemblance of form (homeomorphism), but also by the faculty of entering into analogous reactions, which is not the case with RNO_3 and RCO_3 . The most important and direct method of recognising perfect isomorphism—that is, the absolute analogy of two compounds—is given by that property of

¹ For instance the analogy of the sulphates of K, Rb, and Cs (Chap. XIII., note 1).

^{1a} The crystalline forms of aragonite, strontianite, and witherite belong to the rhombic system; the angle of the prism is, for $CaCO_3$ $116^\circ 10'$, for $SrCO_3$ $117^\circ 19'$, and for $BaCO_3$ $118^\circ 30'$. On the other hand the crystalline forms of calc spar, magnesite, and calcamine, which resemble each other quite as closely, belong to the rhombohedral system, with the angle of the rhombohedron for $CaCO_3$ $105^\circ 8'$, $MgCO_3$ $107^\circ 10'$, and $ZnCO_3$ $107^\circ 40'$. From this comparison it is at once evident that zinc is more closely allied to magnesium than magnesium to calcium.

analogous compounds of separating from solutions in homogeneous crystals, containing the most varied proportions of the analogous substances which enter into their composition. These quantities do not seem to be in dependence on the molecular or atomic weights, and if they are governed by any laws they must be analogous to those which apply to indefinite chemical compounds.² This will be clear from examples. Potassium chloride and potassium nitrate are not isomorphous with each other, and are in an atomic sense composed in a different manner. If these salts be mixed in a solution and the latter evaporated, independent crystals of the two salts will separate, each in that crystalline form which is proper to it. The crystals will not contain a mixture of the two salts. But if we mix the solutions of two isomorphous salts together, then, under certain circumstances, crystals will be obtained which contain both these substances. However, this cannot be taken as an absolute rule, for if we take a solution saturated at a high temperature with a mixture of potassium and sodium chlorides, on evaporation only sodium chloride will separate, and on cooling only potassium chloride. The first will contain very little potassium chloride, and the latter very little sodium chloride.³ But if we take,

² Solutions furnish the commonest examples of indefinite chemical compounds. But the isomorphous mixtures which are so common among the crystalline compounds of silica forming the crust of the earth, as well as alloys, which are so important in the application of metals to the arts, are also instances of indefinite compounds. And if in Chap. I., and in many other portions of this work, it has been necessary to admit the presence of transitions to definite compounds (in a state of dissociation) in solutions, the same applies with even greater force to isomorphous mixtures and alloys. For this reason in many places in this work I refer to facts which compel us to recognise the existence of definite chemical compounds in all isomorphous mixtures and alloys. This view of mine (which dates from the sixties) upon isomorphous mixtures finds a particularly clear confirmation in the researches of B. Roozeboom (1892) (and in those of many others) upon the solubility and crystallising capacity of mixtures of the chlorates of potassium and thallium, KClO_3 and TlClO_3 . He showed that when a solution contains different amounts of these salts, it deposits crystals containing either an excess of the first salt, from 98 per cent. to 100 per cent., or an excess of the second salt, from 68.7 to 100 per cent.; that is, in the crystalline form, either the first salt saturates the second, or the second the first, just as in the solution of ether in water; moreover, the solubilities of the mixtures containing respectively 36.3 and 98 per cent. of KClO_3 are the same, just as the vapour pressure of a saturated solution of water in ether is equal to that of a saturated solution of ether in water (Chap. I., note 47). But just as there are solutions miscible in all proportions, so also certain isomorphous bodies can be present in crystals in all possible proportions of their component parts. Van't Hoff calls such systems 'solid solutions.' These views were subsequently elaborated by Nernst (1892), and Witt (1891) applied them in explaining the phenomena observed in the coloration of tissues.

³ The cause of the differences observed in different compounds of the same type, with respect to their property of forming isomorphous mixtures, must not be looked for in the difference of their volumetric composition, as has been affirmed by many investigators, including Kopp. The molecular volumes (found by dividing the molecular weight by the density) of these isomorphous substances which give intermixtures are not nearer to each other than the volumes of those which do not give such mixtures; for

for example, a mixture of solutions of magnesium sulphate and zinc sulphate, they cannot be separated from each other by evaporating the mixture, notwithstanding the rather considerable difference in solubility of these salts. Again, the isomorphous salts, magnesium carbonate and calcium carbonate, are found together—that is, in one crystal—in nature. The angle of the rhombohedron of these magnesia-lime spars is intermediate between the angles proper to the two separate spars (for calcium carbonate, the angle of the rhombohedron is $105^{\circ} 8'$; for magnesium carbonate, $107^{\circ} 30'$; and for $\text{CaMg}(\text{CO}_3)_2$, $106^{\circ} 10'$). Certain of these **isomorphous mixtures** of calc and magnesia spars appear in well-formed crystals, and in this case there not infrequently exists a simple molecular proportion of strictly definite chemical combination between the component salts—for instance, $\text{CaCO}_3, \text{MgCO}_3$ —whilst in other cases, especially in the absence of distinct crystallisation (in dolomites), no such simple molecular proportion is observable: this is also the case in many artificially prepared isomorphous mixtures. The microscopical and crystallo-optical researches of Professor Inostrant-zoff and others show that in many cases there is really a mechanical, although microscopically minute, juxtaposition in one whole of heterogeneous crystals of calcium carbonate (double refracting) and of the compound CaMgC_2O_6 . If we suppose the adjacent parts to be microscopically small (on the basis of the researches of Mallard, Wyrouboff, and others), we obtain an idea of an isomorphous mixture. The composition of isomorphous mixtures is expressed by formulæ of general type; for instance, for spars, RCO_3 , where $\text{R} = \text{Mg}, \text{Ca}$, and where it may be $\text{Fe}, \text{Mn}, \dots$, &c. This means that the Ca is partially replaced by Mg or another metal. Alums form a common example of the separation of isomorphous mixtures from solutions. They are double sulphates of alumina (or oxides isomorphous with it) and the alkalis, which crystallise in well-formed crystals. If aluminium sulphate is mixed with potassium sulphate, an alum separates, having the composition $\text{KAlS}_2\text{O}_8, 12\text{H}_2\text{O}$. If sodium sulphate or ammonium

example, for magnesium carbonate the combining weight is 84, the density 3.06, and the volume therefore 27; for calcium carbonate in the form of calc spar the volume is 37, and in the form of aragonite 33; for strontium carbonate 41, for barium carbonate 46; that is, the volume of these closely allied isomorphous substances increases with the combining weight. The same is observed if we compare sodium chloride (molecular volume = 27) with potassium chloride (volume = 37), or sodium sulphate (volume = 55) with potassium sulphate (volume = 66), or sodium nitrate (39) with potassium nitrate (48), although the latter are less capable of giving isomorphous mixtures than the former. It is evident that the cause of isomorphism cannot be explained by an approximation in the molecular volumes. It is more likely that, given a similarity in form and composition, the faculty to give isomorphous mixtures is connected with the degree of solubility and its variations. This view is supported by certain data belonging to the province of physical chemistry.

sulphate or rubidium (or thallium) sulphate be used, we obtain alums having the composition $\text{RAlS}_2\text{O}_8, 12\text{H}_2\text{O}$. Not only do they all crystallise in the cubic system, but they also contain an equal molecular quantity of water of crystallisation ($12\text{H}_2\text{O}$). Besides which, if we mix solutions of the potassium and ammonium ($\text{NH}_4\text{AlS}_2\text{O}_8, 12\text{H}_2\text{O}$) alums together, the crystals which separate will contain various proportions of the alkalis taken, and separate crystals of the alums of one or the other kind will not be obtained, but each separate crystal will contain both potassium and ammonium. Nor is this all; if we take a crystal of potassium alum and immerse it in a solution capable of yielding ammonia alum, the crystal of the potash alum will continue to grow and increase in size in this solution—that is, a layer of the ammonia or other alum will deposit itself upon the planes bounding the crystal of the potash alum. This is very distinctly seen if a colourless crystal of a common alum is immersed in a saturated violet solution of chrome alum, $\text{KCrS}_2\text{O}_8, 12\text{H}_2\text{O}$, which then deposits itself in a violet layer over the colourless crystal of the alumina alum, as was observed even before Mitscherlich noticed it. If this crystal be then immersed in a solution of an alumina alum, a layer of this salt will form over the layer of chrome alum, so that one alum is able to incite the growth of the other. If the deposition proceed simultaneously, the resultant intermixture may be minute and inseparable, but its nature is understood from the preceding experiments; the attractive force of crystallisation of isomorphous substances is so nearly equal that the attractive power of an isomorphous substance induces a crystalline superstructure exactly the same as would be produced by the attractive force of like crystalline particles. From this it is evident that one isomorphous substance may induce the crystallisation⁴ of another. Such a phenomenon explains, on the one hand, the aggregation of different isomorphous substances in one crystal, while, on the other hand, it serves as an indication of the nearness both of the molecular composition of isomorphous substances and of those forces which are proper to the elements distinguishing isomorphous substances. Thus, for example, ferrous sulphate or green vitriol crystallises in the monoclinic system, and contains seven molecules of water, $\text{FeSO}_4, 7\text{H}_2\text{O}$, whilst copper vitriol crystallises with five molecules of water in the triclinic system, $\text{CuSO}_4, 5\text{H}_2\text{O}$; nevertheless, it may be easily proved that both salts are perfectly isomorphous; that they are able to appear in identically the same forms and with equal molecular amounts of water. Marignac, by

⁴ A phenomenon of a similar kind is shown for magnesium sulphate in note 27 of the last chapter. In the same example we see what complications the phenomena of dimorphism may introduce when the forms of analogous compounds are compared.

evaporating a mixture of sulphuric acid and ferrous sulphate under the receiver of an air-pump, first obtained crystals of the heptahydrated salt, and then of the pentahydrated salt $\text{FeSO}_4 \cdot 5\text{H}_2\text{O}$, which were perfectly similar to the crystals of copper sulphate. Further, Lecoq de Boisbaudran, by immersing crystals of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in a supersaturated solution of copper sulphate, caused the latter to deposit in the same form as ferrous sulphate, in crystals of the monoclinic system, $\text{CuSO}_4 \cdot 7\text{H}_2\text{O}$.

Hence it is evident that isomorphism—that is, the analogy of forms and the property of inducing crystallisation—may serve as a means for the discovery of analogies in molecular composition. We will take an example in order to render this clear. If, instead of aluminium sulphate, we add magnesium sulphate to potassium sulphate, then, on evaporating the solution, the double salt $\text{K}_2\text{MgS}_2\text{O}_8 \cdot 6\text{H}_2\text{O}$ (Chap. XIV., note 28) separates instead of an alum, and the ratio of the component parts (in alums one atom of potassium per 2SO_4 , and here two atoms) and the amount of water of crystallisation (in alums 12, and here 6 equivalents per 2SO_4) are quite different; nor is this double salt in any way isomorphous with the alums, nor capable of forming an isomorphous crystalline mixture with them, nor does the one salt provoke the crystallisation of the other. From this we must conclude that although alumina and magnesia, or aluminium and magnesium, resemble each other, they are not isomorphous, and that although they give partially similar double salts, these salts are not analogous to each other. And this is expressed in their chemical formulæ by the fact that the number of atoms in alumina or aluminium oxide, Al_2O_3 , is different from the number in magnesia, MgO . Aluminium is trivalent and magnesium bivalent. Thus, having obtained a double salt from a given metal, it is possible to judge of the analogy of the given metal with aluminium or with magnesium, or of the absence of such an analogy, from the composition and form of this salt. Thus zinc, for example, does not form alums, but forms with potassium sulphate a double salt having a composition exactly like that of the corresponding salt of magnesium. It is often possible to distinguish the bivalent metals analogous to magnesium or calcium from the trivalent metals, like aluminium, by such a method. Furthermore, the specific heat and vapour density serve as guides. There are also indirect proofs. Thus iron gives ferrous compounds, FeX_2 , which are isomorphous with the compounds of magnesium, and ferric compounds, FeX_3 , which are isomorphous with the compounds of aluminium; in this instance the relative composition is directly determined by analysis, because, for a given amount of iron, FeCl_2 only contains two-thirds of the amount of

chlorine which occurs in FeCl_3 , and the composition of the corresponding oxygen compounds, i.e., of ferrous oxide, FeO , and ferric oxide, Fe_2O_3 , clearly indicates the analogy of ferrous oxide with MgO and that of ferric oxide with Al_2O_3 .

Thus in the building up of similar molecules in crystalline forms we see one of the numerous means for judging of the internal world of molecules and atoms. This method ⁵ has more than once been employed

⁵ The property of solids of occurring in regular crystalline forms—the occurrence of many substances in the earth's crust in these forms—and those simple geometrical laws which govern the formation of crystals, long ago attracted the attention of the naturalist to crystals. The crystalline form is, without doubt, the expression of the relation in which the atoms occur in the molecules, and in which the molecules occur in the mass, of a substance. Crystallisation is determined by the distribution of the molecules along the direction of greatest cohesion, and therefore those forces must take part in the crystalline distribution of matter which act between the molecules; and, as they depend on the forces binding the atoms together in the molecules, a very close connection must exist between the atomic composition and the distribution of the atoms in the molecule on the one hand, and the crystalline form of a substance on the other; and hence an insight into the composition may be arrived at from the crystalline form. Such is the elementary and *a priori* idea which lies at the base of all researches into the connection between composition and crystalline form. Haüy, in 1811, established the following fundamental law, which has been worked out by later investigators: The fundamental crystalline form for a given chemical compound is constant (only the combinations vary), and with a change of composition the crystalline form also changes, naturally with the exception of such limiting forms as the cube, regular octahedron, &c., which may belong to various substances of the regular system. The fundamental form is determined by the angles of certain fundamental geometric forms (prisms, pyramids, rhombohedra), or the ratio of the crystalline axes, and is connected with the optical and many other properties of crystals. Since the establishment of this law the description of definite compounds in a solid state is accompanied by a description (measurement) of its crystals, which forms an invariable, definite, and measurable character. The most important epochs in the further history of this question were made by the following discoveries:—*Klaproth*, *Vauquelin*, and others showed that aragonite has the same composition as calc spar, whilst the former belongs to the rhombic and the latter to the hexagonal system. Haüy at first considered that the composition, and after that the arrangement, of the atoms in the molecules was different. This is dimorphism (see Chap. XIV., note 46). *Beudant*, *Frankenheim*, *Laurent*, and others found that the forms of the two nitrates, KNO_3 and NaNO_3 , exactly correspond with the forms of aragonite and calc spar; that they are able, moreover, to pass from one form into another; and that the difference of the forms is accompanied by a small alteration of the angles, for the angle of the prisms of potassium nitrate and aragonite is 119° , and that of sodium nitrate and calc spar, 120° ; and therefore **dimorphism**, or the crystallisation of one substance in different forms, does not necessarily imply a great difference in the distribution of the molecules, although some difference clearly exists. The researches of *Mitscherlich* (1822) on the dimorphism of sulphur confirmed this conclusion, although it cannot yet be affirmed that in dimorphism the arrangement of the atoms remains unaltered, and that only the molecules are distributed differently. *Leblanc*, *Berthier*, *Wollaston*, and others already knew that many substances of different composition appear in the same forms, and crystallise together in one crystal. *Gay-Lussac* (1816) showed that crystals of potash alum continue to grow in a solution of ammonia alum. *Beudant* (1817) explained this phenomenon as the **assimilation** of a foreign substance by a substance having a great force of crystallisation, which he illustrated by many natural and artificial examples. But *Mitscherlich*, and afterwards *Berzelius* and *Heinrich Rose*

for discovering the analogy of elements and of their compounds; and as crystals are measurable, and their ability to form crystalline mix-

and others, showed that such an assimilation only exists with a similarity or approximate similarity of the forms of the individual substances and with a certain degree of chemical analogy. Thus was established the idea of **isomorphism** as an analogy of forms by reason of a resemblance of atomic composition, and by it was explained the variability of the composition of a number of minerals as isomorphous mixtures. Thus all the garnets are expressed by the general formula: $(RO)_3M_2O_3(SiO_2)_3$, where $R=Ca, Mg, Fe, Mn$, and $M=Fe, Al$, and where we may have either R and M separately, or their equivalent compounds, or their mixtures in all possible proportions.

But other facts, which render the correlation of form and composition still more complex, have accumulated side by side with a mass of data which may be accounted for by isomorphism and dimorphism. Foremost among the former stand the phenomena of **homeomorphism**—that is, a nearness of forms with a difference of composition—and then the cases of polymorphism and hemimorphism—that is, a nearness of the fundamental forms or only of certain angles for substances which are near or analogous in their composition. Instances of homeomorphism are very numerous. Many of these, however, may be reduced to a resemblance of atomic composition, although they do not correspond to an isomorphism of the component elements; for example, CdS (greenockite) and AgI , $CaCO_3$ (aragonite) and KNO_3 , $CaCO_3$ (calc spar) and $NaNO_3$, $BaSO_4$ (heavy spar), $KMnO_4$ (potassium permanganate), and $KClO_4$ (potassium perchlorate), Al_2O_3 (corundum) and $FeTiO_3$ (titanic iron ore), FeS_2 (marcasite, rhombic system) and $FeSAs$ (arsenical pyrites), NiS and $NiAs$, &c. But besides these instances, there are homeomorphous substances with an absolute dissimilarity of composition. Many such instances were pointed out by *Dana*. *Cinnabar*, HgS , and *susaunite*, $PbSO_4 \cdot 3PbCO_3$, appear in closely analogous crystalline forms; the acid potassium sulphate crystallises in the monoclinic system in crystals analogous to feldspar, $KAlSi_3O_8$; *glauberite*, $Na_2Ca(SO_4)_2$, *augite* $RSiO_3$ ($R=Ca, Mg$), *sodium carboxate*, $Na_2CO_3 \cdot 10H_2O$, *Glauber's salt*, $Na_2SO_4 \cdot 10H_2O$ and *borax*, $Na_2BrO_7 \cdot 10H_2O$, not only belong to the same system (monoclinic), but exhibit an analogy of combinations and approximately the same corresponding angles. These and many other similar cases might appear to be perfectly arbitrary (especially as a similarity of angles and fundamental forms is a relative idea) were there not other cases where a resemblance of properties and a distinct relation in the variation of composition is connected with a resemblance of form. Thus, for example, *alumina*, Al_2O_3 and water, H_2O , are frequently found in many pyroxenes and amphiboles which only contain silica and *magnesia* (MgO , CaO , FeO , MnO). *Scheerer* and *Hermann*, and many others, endeavoured to explain such instances by **polymetric isomorphism**, stating that MgO may be replaced by $3H_2O$ (for example, *olivine* and *serpentine*), SiO_2 by Al_2O_3 (in the amphiboles, *tales*) and so on. A certain number of the instances of this order are subject to doubt, because many of the natural minerals which serve as the basis for the establishment of polymetric isomorphism, in all probability, no longer present their original composition, but one altered under the influence of solutions which have come into contact with them; they therefore belong to the class of **pseudomorphs**, or false crystals. There is, however, no doubt of the existence of a whole series of natural and artificial homeomorphs, which differ from each other by molecular proportions of water, silica, and some other component parts. Thus, *Thomsen* (1874) showed a very striking instance. The metallic chlorides, RCl_2 , often crystallise with water, and they do not then contain less than one molecule of water per atom of chlorine. The most familiar representative of the order $RCl_2 \cdot 2H_2O$ is $BaCl_2 \cdot 2H_2O$, which crystallises in the rhombic system. Barium bromide, $BaBr_2 \cdot 2H_2O$, and copper chloride, $CuCl_2 \cdot 2H_2O$, have nearly the same forms. Potassium iodate, KIO_4 ; potassium chlorate, $KClO_4$; potassium permanganate, $KMnO_4$; barium sulphate, $BaSO_4$; calcium sulphate, $CaSO_4$; sodium sulphate, Na_2SO_4 ; barium formate, $BaC_2H_3O_4$, and others have almost the same crystalline form (of the rhombic system). Parallel with this series are those of the metallic chlorides of the form $RCl_3 \cdot 4H_2O$,

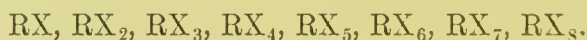
tures can be experimentally verified, this method is an objective one, and, as such, is in no sense arbitrary.

of the sulphates of the composition $\text{RSO}_4 \cdot 2\text{H}_2\text{O}$, and of the formates $\text{RC}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$. These compounds belong to the monoclinic system, have a close resemblance of form, and differ from the first series by containing two more molecules of water. The addition of two more molecules of water in all the above series also gives forms of the monoclinic system closely resembling each other; for example, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$. Hence we see that not only is $\text{RCl}_2 \cdot 2\text{H}_2\text{O}$ analogous in form to RSO_4 and $\text{RC}_2\text{H}_2\text{O}_4$, but that their compounds with $2\text{H}_2\text{O}$ and with $4\text{H}_2\text{O}$ also exhibit closely analogous forms. From these examples it is evident that the conditions which determine a given form may be repeated not only in the presence of an isomorphous exchange—that is, with an equal number of atoms in the molecule—but also in the presence of an unequal number when there are peculiar and as yet ungeneralised relations in composition. Thus ZnO and Al_2O_3 exhibit a close analogy of form. Both oxides belong to the rhombohedral system, and the angle between the pyramid and the terminal plane is in the first $118^\circ 7'$, and in the second $118^\circ 49'$. Alumina, Al_2O_3 , is also analogous in form to SiO_2 , and we shall see that these analogies of form are conjoined with a certain analogy in properties. It is not surprising, therefore, that in the complex molecule of a silicious compound it is sometimes possible to replace SiO_2 by means of Al_2O_3 , as Scheerer admits. The oxides Cu_2O , MgO , NiO , Fe_3O_4 , CeO_2 , crystallise in the regular system, although they are of very different atomic structure. *Marignac* demonstrated the perfect analogy of the forms of K_2ZrF_6 and CaCO_3 , and the former is even dimorphous, like calcium carbonate. The same salt is isomorphous with R_2NbOF_5 and $\text{R}_2\text{WO}_2\text{F}_4$, where R is an alkali metal. There is an equivalency between CaCO_3 and K_2ZrF_6 , because K_2 is equivalent to Ca, C to Zr, and F_6 to O_3 , and with the isomorphism of the other two salts we find besides an equal content of the alkali metal—an equal number of atoms on the one hand and an analogy to the properties of K_2ZrF_6 on the other. The long-known isomorphism of the corresponding compounds of potassium and ammonium, KX and NH_4X , may be taken as the simplest example of the fact that an analogy of form shows itself with an analogy of chemical reaction even without an equality in atomic composition. Therefore the ultimate progress of the entire doctrine of the correlation of composition and crystalline forms will only be arrived at with the accumulation of a sufficient number of facts collected on a plan corresponding with the problems which here present themselves. The first steps have already been made. The researches of the Geneva savant, *Marignac*, on the crystalline form and composition of many of the double fluorides, and the work of *Wyrouboff* on the ferricyanides and other compounds, are particularly important in this respect.

It is already evident that, with a definite change of composition, certain angles remain constant, notwithstanding that others are subject to alteration. Such an instance of the relation of forms was observed by *Laurent*, and named by him **hemimorphism** (an anomalous term) when the analogy is limited to certain angles, and **paramorphism** when the forms in general approach each other, but belong to different systems. Thus, for example, the angle of the planes of a rhombohedron may be greater or less than 90° , and therefore such acute and obtuse rhombohedra may closely approximate to the cube. Hausmannite, Mn_3O_4 , belongs to the tetragonal system, and the planes of its pyramid are inclined at an angle of about 118° , whilst magnetic iron ore, Fe_3O_4 , which resembles hausmannite in many respects, appears in regular octahedra—that is, the pyramidal planes are inclined at an angle of $109^\circ 28'$. This is an example of paramorphism; the systems are different, the compositions are analogous, and there is a certain resemblance in form. Hemimorphism has been found in many instances of saline and other substitutions. Thus, *Laurent* demonstrated, and *Hintze* confirmed (1873), that naphthalene derivatives of analogous composition are hemimorphous. *Nicklès* (1849) showed that in ethylene sulphate the angle of the prism is $125^\circ 26'$, and in the nitrate of the same radicle $126^\circ 95'$. The angle of the prism of methylamine oxalate is $131^\circ 20'$, and with the fluoride, which is very different in composition from the former, the angle is 132°

The regularity and simplicity expressed by the exact laws of crystalline form repeat themselves in the aggregation of the atoms to form molecules. Here, as there, there are but few forms which are essentially different, and their apparent diversity reduces itself to a few fundamental differences of type. There the molecules aggregate themselves into crystalline forms; here, the atoms aggregate themselves into molecular forms or into **the types of compounds**. In both cases the fundamental crystalline or molecular forms are liable to variations, conjunctions, and combinations. If we know that potassium gives compounds of the fundamental type KX , where X is a univalent element (which combines with one atom of hydrogen, and is, according to the law of substitution, able to replace it), then we know the composition of its compounds: K_2O , KHO , KCl , NH_2K , KNO_3 , K_2SO_4 , $KHSO_4$, $K_2Mg(SO_4)_2 \cdot 6H_2O$, &c. All the possible derivative crystalline forms are not known. So also all the atomic combinations are not known for every element. Thus in the case of potassium, KCH_3 , K_3P , K_2Pt , and other like compounds which exist for hydrogen or chlorine are unknown.

The majority of the fundamental types for the building up of atoms into molecules are already known to us. If X stand for a univalent element, and R for an element combined with it, then eight atomic types may be observed:—



Groth (1870) endeavoured to indicate in general what kinds of change of form proceed with the substitution of hydrogen by various other elements and groups, and he observed a regularity which he termed **morphotropy**. The following examples show that morphotropy recalls the hemimorphism of Laurent. Benzene, C_6H_6 , rhombic system, ratio of the axes $0.891 : 1 : 0.799$. Phenol, $C_6H_5(OH)$, and resorcinol, $C_6H_4(OH)_2$, also rhombic system, but one axial ratio is changed, the numbers for resorcinol being $0.910 : 1 : 0.540$ —that is, a portion of the crystalline structure in one direction is the same, but in the other direction it is changed, whilst in the rhombic system dinitrophenol, $C_6H_3(NO_2)_2(OH) = 0.833 : 1 : 0.753$; trinitrophenol (picric acid), $C_6H_2(NO_2)_3(OH) = 0.937 : 1 : 0.974$; and the potassium salt $= 0.942 : 1 : 1.354$. Here the ratio of the first pair of axes is preserved—that is, certain angles remain constant, and the chemical proximity of the composition of these bodies is undoubted. Laurent compares hemimorphism with architectural style. Thus, Gothic cathedrals differ in many respects, but there is an analogy expressed both in the sum total of their common relations and in certain details—for example, in the windows. It is evident that we may expect many fruitful results for molecular mechanics (which forms a problem common to many provinces of natural science) from the further elaboration of the data concerning those variations which take place in crystalline form when the composition of a substance is subjected to a known change, and I therefore consider it useful to point out to the student of science seeking for matter for independent scientific research this vast field for work which is presented by the correlation of form and composition. The geometrical regularity and varied beauty of crystalline forms offer no small attraction to research of this kind.

Let X be chlorine or hydrogen. Then examples of the first type will be : H_2 , Cl_2 , HCl , KCl , $NaCl$, &c. The compounds of oxygen or calcium may serve as examples of the type RX_2 : OH_2 , OCl_2 , $OHCl$, CaO , $Ca(OH)_2$, $CaCl_2$, &c. For the third type RX_3 we know the representative NH_3 and the corresponding compounds N_2O_3 , $NO(OH)$, $NO(OK)$, PCl_3 , P_2O_3 , PH_3 , SbH_3 , Sb_2O_3 , B_2O_3 , BCl_3 , Al_2O_3 , &c. The type RX_4 is known among the hydrogen compounds. Marsh gas, CH_4 , and its corresponding saturated hydrocarbons, C_nH_{2n+2} , are the best representatives. Also CH_3Cl , CCl_4 , $SiCl_4$, $SnCl_4$, SnO_2 , CO_2 , SiO_2 , and a whole series of other compounds come under this class. The type RX_5 is also already familiar to us, but there are no purely hydrogen compounds among its representatives. Sal-ammoniac, NH_4Cl , and the corresponding $NH_4(OH)$, $NO_2(OH)$, $ClO_2(OK)$, as well as PCl_5 , $POCl_3$, &c., are representatives of this type. In the higher types also there are no hydrogen compounds, but in the type RX_6 there is the chlorine compound WCl_6 , and a fluorine one, SF_6 . However, there are many oxygen compounds, and among them SO_3 is the best known representative. To this class also belong $SO_2(OH)_2$, SO_2Cl_2 , $SO_2(OH)Cl$, CrO_3 , &c., all of an acid character. Of the higher types there are in general only oxygen and acid representatives. The type RX_7 we know in perchloric acid, $ClO_3(OH)$, and potassium permanganate, $MnO_3(OK)$, is also a member. The type RX_8 in a free state is very rare; osmic anhydride, OsO_4 , is the best known representative of it.⁶

⁶ The still more complex combinations—which are so clearly expressed in the crystallo-hydrates, double salts, and similar compounds—although they may be regarded as independent, are, however, most easily understood with our present knowledge as aggregations of whole molecules to which there are no corresponding double compounds, containing one atom of an element R and many atoms of other elements RX_n . The above types embrace all cases of direct combinations of atoms, and the formula $MgSO_4 \cdot 7H_2O$ cannot, without violating known facts, be directly deduced from the types MgX_n or SX_n , whilst the formula $MgSO_4$ corresponds both with the type of the magnesium compounds MgX_2 and with the type of the sulphur compounds SO_2X_2 , or in general SX_6 , where X_2 is replaced by $(OH)_2$, with the substitution in this case of H_2 by the atom Mg, which always replaces H_2 . However, it must be remarked that the sodium crystallo-hydrates often contain $10H_2O$, the magnesium crystallo-hydrates 6 and $7H_2O$, and that the type PtM_2X_6 is proper to the double salts of platinum, &c. With the further development of our knowledge concerning crystallo-hydrates, double salts, alloys, solutions, &c., in the chemical sense of feeble compounds (that is, such as are easily destroyed by feeble chemical influences) it will probably become possible to arrive at a perfect generalisation for them. For a long time these subjects were only studied by the way or by chance; our knowledge of them is accidental and destitute of system, and it is therefore impossible to expect as yet any generalisation as to their nature. It is not long since the days of Gerhardt when only three types were recognised : RX , RX_2 , and RX_3 ; the type RX_4 was afterwards added (by Cooper, Kekulé, Butleroff, and others), mainly for the purpose of generalising the data respecting the carbon compounds. And indeed many are still satisfied with these types, and derive the higher types from them; for instance, RX_5 from RX_3 —as, for example, $POCl_3$, from PCl_3 , considering the oxygen

The four lower types RX , RX_2 , RX_3 , and RX_4 are met with in compounds of the elements R with chlorine and oxygen, and also in their compounds with hydrogen, whilst the four higher types only appear for such acid compounds as are formed by chlorine, oxygen, and similar elements. Among the oxygen compounds the **saline oxides** which are capable of forming salts either through the function of a base or through the function of an acid oxide attract the greatest interest in every respect. Certain elements, like calcium and magnesium, only give one saline oxide—for example, MgO , corresponding with the type MgX_2 . But the majority of the elements appear in several such forms. Thus copper gives CuX and CuX_2 , or Cu_2O and CuO . If an element R gives a higher type RX_n , then there often also exist, as if by symmetry, lower types, RX_{n-2} , RX_{n-4} , and in general such types as differ from RX_n by an even number of X . Thus in the case of sulphur the types SX_2 , SX_4 , and SX_6 are known—for example, SH_2 , SO_2 , and SO_3 . The last type is the highest, SX_6 . The types SX_5 and SX_3 do not exist. But even and uneven types sometimes appear for one and the same element. Thus the types RX and RX_2 are known for copper and mercury.

Among the **saline oxides** only the **eight types** enumerated below are known to exist. They determine the possible formulæ of the compounds of the elements, if it be taken into consideration that an element which gives a certain type of combination may also give lower types. For this reason the rare type of the **suboxides** or *quaternary* oxides R_4O (for instance, Ag_4O , Ag_2Cl) is not characteristic; it is always accompanied by one of the higher grades of oxidation, and the compounds of this type are distinguished by their great chemical instability, and split up into an element and the higher compound (for instance, $Ag_4O = 2Ag + Ag_2O$). Many elements, moreover, form transition oxides, which have an intermediate composition and are able, like N_2O_4 , to split up into the lower and higher oxides. Thus iron gives magnetic oxide, Fe_3O_4 , which is in all respects (by its reactions) a compound of the suboxide FeO with the oxide Fe_2O_3 .

to be bound both to the chlorine (as in $HClO$) and to the phosphorus. But the time has now arrived when it is clearly seen that the forms RX , RX_2 , RX_3 , and RX_4 do not exhaust the whole variety of phenomena. The revolution became evident when Würtz showed that PCl_5 is not a compound of $PCl_3 + Cl_2$ (although it may decompose into two molecules), but a whole molecule capable of passing into vapour as PCl_5 like PF_5 and SiF_4 . The time for the recognition of types even higher than RX_8 is in my opinion in the future; that it will come we can already see in the fact that oxalic acid, $C_2H_2O_4$, gives a crystallo-hydrate with $2H_2O$, which may be referred to the type CH_4 , or rather to the type of ethane, C_2H_6 , all the atoms of hydrogen of which are replaced by hydroxyl, $C_2H_2O_4 \cdot 2H_2O = C_2(OH)_6$ (see Chap. XXII., note 35).

The independent and more or less stable saline compounds correspond with the following eight types :—

R_2O ; salts RX , hydroxides ROH . Generally basic like K_2O , Na_2O , Hg_2O , Ag_2O , Cu_2O ; though there are acid oxides of this composition, they are very rare, are only formed by distinctly acid elements, and even then have only feeble acid properties ; for example, Cl_2O and N_2O .

R_2O_2 or RO ; salts RX_2 , hydroxides $R(OH)_2$. The most simple basic salts R_2OX_2 or $R(OH)X$; for instance, the chloride Zn_2OCl_2 ; also an almost exclusively basic type ; but the basic properties of the oxides of this type are more feebly developed than in the preceding type. For example, CaO , MgO , BaO , PbO , FeO , MnO , &c.

R_2O_3 ; salts RX_3 , hydroxides $R(OH)_3$, $RO(OH)$, the most simple basic salts ROX , $R(OH)X_3$. The bases are feeble, like Al_2O_3 , Fe_2O_3 , Tl_2O_3 , Sb_2O_3 . The acid properties are also feebly developed ; for instance, in B_2O_3 ; but with the non-metals the properties of acids are already clear ; for instance, P_2O_3 , $P(OH)_3$.

R_2O_4 or RO_2 ; salts RX_4 or ROX_2 , hydroxides $R(OH)_4$, $RO(OH)_2$. Rarely bases (feeble), like ZrO_2 , PtO_2 ; more often acid oxides ; but the acid properties are in general feeble, as in CO_2 , SO_2 , SnO_2 . Many intermediate oxides appear in this and the preceding and following types.

R_2O_5 ; salts principally of the types ROX_3 , RO_2X , $RO(OH)_3$, $RO_2(OH)$, rarely RX_5 . The basic character is feeble ; the acid character predominates, as is seen in N_2O_5 , P_2O_5 , Cl_2O_5 , and then $X = OH$, OK , &c. ; for example, $NO_2(OK)$.

R_2O_6 or RO_3 ; salts and hydroxides generally of the type RO_2X_2 , $RO_2(OH)_2$. Oxides of an acid character, as SO_3 , CrO_3 , MnO_3 . Basic properties rare and feebly developed as in UO_3 .

R_2O_7 ; salts of the form RO_3X , $RO_3(OH)$, acid oxides ; for instance, Cl_2O_7 , Mn_2O_7 . Basic properties as feebly developed as the acid properties in the oxides R_2O .

R_2O_8 or RO_4 . A very rare type, and only known in OsO_4 and RuO_4 .

The majority of the ordinary elements appear in the first seven types, and if a given element gives oxides of one of the higher types, it is also able to form all the lower oxides ; for example, nitrogen.

It is evident from the circumstance that in all the higher types the **acid hydroxides** (for example, $HClO_4$, H_2SO_4 , H_3PO_4) and salts with a single atom of one element **contain**, like the higher saline type RO_4 , **not more than four atoms of oxygen** ; that the formation of the saline oxides is governed by a certain common principle which

is best looked for in the fundamental properties of oxygen, and in general of the most simple compounds. The hydrate of the oxide RO_2 is of the higher type $\text{RO}_2, 2\text{H}_2\text{O} = \text{RH}_4\text{O}_4 = \text{R}(\text{HO})_4$. Such, for example, is the hydrate of silica and the salts (orthosilicates) corresponding with it, $\text{Si}(\text{MO})_4$. The oxide R_2O_5 corresponds with the hydrate $\text{R}_2\text{O}_5, 3\text{H}_2\text{O} = 2\text{RH}_3\text{O}_4 = 2\text{RO}(\text{OH})_3$. Such is orthophosphoric acid, PH_3O_4 . The hydrate of the oxide RO_3 is $\text{RO}_3, \text{H}_2\text{O} = \text{RH}_2\text{O}_4 = \text{RO}_2, (\text{OH})_2$ —for instance, sulphuric acid. The hydrate corresponding to R_2O_7 is evidently $\text{RHO}_4 = \text{RO}_3(\text{OH})$ —for example, perchloric acid. Here, besides containing O_4 , it must further be remarked that **the amount of hydrogen in the hydrate is equal to the amount of hydrogen in the hydrogen compound**. Thus silicon gives SiH_4 and SiH_4O_4 , phosphorus PH_3 and PH_3O_4 , sulphur SH_2 and SH_2O_4 , chlorine ClH and ClHO_4 . This connects in a harmonious and general system the fact that **the elements are capable of combining with a greater amount of oxygen, the less the amount of hydrogen which they are able to retain**. In this the key to the comprehension of all further deductions must be looked for, and we shall therefore formulate this rule in general terms. An element R gives a hydrogen compound RH_n , the hydrate of its higher oxide will be RH_nO_4 , and therefore the higher oxide will contain $2\text{RH}_n\text{O}_4 - n\text{H}_2\text{O} = \text{R}_2\text{O}_{8-n}$. For example, chlorine gives $\text{ClH}(n=1)$, the hydrate ClHO_4 , and the higher oxide Cl_2O_7 . Carbon gives CH_4 and CO_2 . So, also, SiO_2 and SiH_4 are the higher compounds of silicon with hydrogen and oxygen, like CO_2 and CH_4 . Here the amounts of oxygen and hydrogen are equivalent. Nitrogen combines with a large amount of oxygen, forming N_2O_5 , but, on the other hand, with a small quantity of hydrogen in NH_3 . *The sum of the equivalents of hydrogen and oxygen, occurring in combination with an atom of nitrogen, is, as always in the higher types, equal to eight*. It is the same with the other elements which combine with hydrogen and oxygen. Thus sulphur gives SO_3 ; consequently, six equivalents of oxygen fall to an atom of sulphur, and in SH_2 two equivalents of hydrogen. The sum is again equal to eight. The relation between Cl_2O_7 and ClH is the same. This shows that the property of elements of combining with such different elements as oxygen and hydrogen is subject to one common law, which is also formulated in the system of the elements presently to be described.⁷ Just as for hydrogen, besides water H_2O , which forms an example of

⁷ Not wishing to complicate the explanation, I only touch here on the general features of the relation between the hydrates and oxides and of the oxides among themselves. Thus, for instance, the conception of the ortho-acids and of the normal acids will be considered in speaking of phosphoric and phosphorous acids.

the saline oxides and the only saline compound of hydrogen, there also exists the peroxide of hydrogen H_2O_2 , with a series of peculiar reactions which distinguish it from the saline oxides, so also the majority of other elements have, often, if not always, besides their corresponding saline oxides, their **peroxides**, containing more oxygen than the higher saline oxides and capable not only of entering into peculiar reactions like those of peroxide of hydrogen, but also of forming peroxide of hydrogen under many circumstances, and often of being formed either from H_2O_2 , or under the same conditions as H_2O_2 .^{7a} A slight acquaintance with bases, acids and salts, and with peroxide of hydrogen, removes all doubt as to whether a given oxide or its hydrate should be referred to the class of saline oxides or of peroxides, even if there be salts corresponding to the peroxide. Persulphuric acid, $\text{H}_2\text{S}_2\text{O}_8$, which possesses the well-marked properties of a peroxide, as will be seen in describing it (Chap. XX.), is an instance in question. What was said above about oxides, and what will be further said respecting them, refers exclusively to the saline oxides, all the more so as the peroxides (and among them persulphuric acid) have been studied far less than the saline oxides and the same grouping and degree of analogy among the elements is seen in their faculty to form peroxides as in the case of true saline oxides.^{7b}

In the preceding relation between the faculty of the elements to combine with oxygen and hydrogen we see not only the regularity and simplicity which govern the formation and properties of the saline oxides and of all the compounds of the elements, but also a fresh and exact means for recognising the analogy between elements. Analogous elements give compounds of analogous types, both higher and lower. If CO_2 and SO_2 are two gases which closely resemble each other both in their physical and chemical properties, the reason of this must be looked for not in an analogy of sulphur and carbon, but in that identity of the type of combination, RX_4 , which both oxides assume, and in that influence which a large mass of oxygen always exerts on the

^{7a} In many such cases taking place in the presence of water, and where the water is retained, it is difficult to say whether the oxygen is held in the peroxide of the element or in the form of peroxide of hydrogen. Thus molybdenum, for instance, gives a higher oxide, MoO_3 , and it also forms a hydrate of the peroxide, $\text{Mo}_2\text{H}_2\text{O}_8 = \text{Mo}_2\text{O}_7 \cdot \text{H}_2\text{O}$. This may, however, be regarded as a compound of oxide of molybdenum with peroxide of hydrogen, $\text{Mo}_2\text{H}_2\text{O}_8 = 2\text{MoO}_3 + \text{H}_2\text{O}_2$, just as compounds of peroxide of hydrogen with BaO_2 , &c., are known (Chap. IV.).

^{7b} There is no doubt that analogous elements very often give analogous peroxides, and a study of the peroxides supports the periodic system of the elements, as the researches of Piccini, Melikoff, Pissarjewsky, and others show. The subject is, however, as yet poor in facts, and the peroxides evince but few direct relations to the radical properties of the elements, and therefore I think that a general systematisation of the peroxides is a matter of the future.

properties of its compounds. In fact, there is little resemblance between carbon and sulphur, as is seen not only from the fact that CO_2 is the *higher form* of oxidation, whilst SO_2 is able to further oxidise into the higher oxide SO_3 , but also from the fact that all the other compounds—for example, SH_2 and CH_4 , SCl_2 and CCl_4 , &c.—are entirely unlike both in type and in chemical properties. This absence of analogy in carbon and sulphur is especially clearly seen in the fact that the highest saline oxides are of different composition, CO_2 for carbon, and SO_3 for sulphur. In Chapter VIII. we considered the limit to which carbon tends in its compounds, and in a similar manner there is for every element a tendency to attain a certain highest **limit** RX_n in its compounds. This view was particularly developed in the middle of the nineteenth century by Frankland in studying the organo-metallic compounds, i.e., those in which X is wholly or partially a hydrocarbon radicle; for instance, $\text{X}=\text{CH}_3$ or C_2H_5 &c. Thus, for example, antimony, Sb (Chap. XIX.) gives, with chlorine, compounds SbCl_3 and SbCl_5 and corresponding oxygen compounds Sb_2O_3 and Sb_2O_5 , whilst under the action of CH_3I , $\text{C}_2\text{H}_5\text{I}$, or in general EI (where E is a hydrocarbon radicle of the paraffin series), upon antimony or its alloy with sodium there are formed SbE_3 (for example, $\text{Sb}(\text{CH}_3)_3$, boiling at about 81°), which, corresponding to the lower form of combination SbX_3 , are able to combine further with EI, or Cl_2 , or O, and to form compounds of the limiting type SbX_5 ; for example, SbE_4Cl , corresponding to NH_4Cl with the substitution of nitrogen by antimony, and of hydrogen by the hydrocarbon radicle. The elements, which are most chemically analogous, are characterised by the fact of their giving compounds of similar form RX_n . The halogens, which are analogous, give both higher and lower compounds.^{7c} So also do the metals of the alkalis and of the alkaline earths. And we saw that this analogy extends to the composition and properties of the carbon, nitrogen, and hydrogen compounds of these metals, as is best seen in the salts. Many such groups of analogous elements have long been known. Thus there are analogues of oxygen, nitrogen, and carbon, and we shall meet with many such groups. But an acquaintance with them inevitably leads to the questions, What is the cause of the analogy and what is the relation of one group to another? If these questions remain

^{7c} The analogy of the types of combination of the halogens is partly destroyed by fluorine, which gives higher types with greater ease than Cl; thus it forms SF_6 (Chap. XX.) with sulphur, and IF_5 with iodine, which chlorine does not. **Pentafluoride of iodine** was obtained by Moissan (1902) by the direct action of fluorine on iodine. It is a colourless liquid which solidifies at $+8^\circ$, boils at 97° without decomposition, and decomposes at about 500° . It is highly hygroscopic, and in general presents many remarkable reactions.

unanswered, it is easy to fall into error in the formation of the groups, because the notions of the degree of analogy will always be relative, and will not present any accuracy or distinctness. Thus lithium is analogous in some respects to potassium and in others to magnesium; beryllium is analogous to both aluminium and magnesium. Thallium, as we shall afterwards see and as was observed on its discovery, has much kinship with lead and mercury, but in some of its properties it resembles lithium and potassium. Naturally, where it is impossible to make measurements one is reluctantly obliged to limit oneself to approximate comparisons, founded on arbitrarily chosen data which are often wanting in exactitude. But in the elements there is one accurately measurable property, which is subject to no doubt—namely, that property which is expressed in their atomic weights. Its magnitude indicates the relative mass of the atom, or, if we avoid the conception of the atom, its magnitude shows the relation between the masses forming the chemical and independent individuals or elements. And according to the teaching of all exact data concerning the phenomena of nature, *the mass of a substance is that property on which all its remaining properties must be dependent*, because they are all determined by similar conditions or by those forces which act in determining the weight of a substance, and this is directly proportional to its mass. Therefore it is most natural to seek for a dependence between the properties and analogies of the elements on the one hand and their atomic weights on the other.

This is the fundamental idea which leads to **arranging all the elements according to their atomic weights**. A periodic repetition of properties is then immediately observed in the elements. We are already familiar with examples of this :—

F = 19,	Cl = 35·5,	Br = 80,	I = 127,
Na = 23,	K = 39,	Rb = 85,	Cs = 133,
Mg = 24,	Ca = 40,	Sr = 87,	Ba = 137.

The essence of the matter is seen in these groups. The halogens have smaller atomic weights than the alkali metals, and the latter than the metals of the alkaline earths. A logical development and generalisation of this fact leads us to conclude that, **if all the elements are arranged in the order of their atomic weights, a periodic repetition of properties is obtained**. This is expressed by the **law of periodicity**; *the properties of the elements, as well as the forms and properties of their compounds, are in periodic dependence on, or (expressing ourselves algebraically) form a periodic function of, the atomic weights of*

*the elements.*⁸ The table of the periodic system of the elements, with the values of the atomic weights proper to them in ascending order,

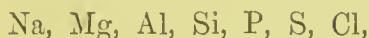
⁸ The periodic law and the periodic system of the elements appeared in the same form as here given in the first edition of this work, begun in 1868 and finished in 1871. In laying out the accumulated information respecting the elements, I had occasion to reflect on their mutual relations. At the beginning of 1869 I distributed among many chemists a pamphlet entitled *An Attempted System of the Elements, based on their Atomic Weights and Chemical Analogies*, and at the March meeting of the Russian Chemical Society, 1869, I communicated a paper *On the Correlation of the Properties and Atomic Weights of the Elements*. The substance of this paper is embraced in the following conclusions: (1) the elements, if arranged according to their atomic weights, exhibit an evident *periodicity* of properties. (2) Elements which are similar as regards their chemical properties have atomic weights which are either of nearly the same value (platinum, iridium, osmium) or which increase regularly (e.g., potassium, rubidium, caesium). (3) The arrangement of the elements or of groups of elements in the order of their atomic weights corresponds with their so-called *valencies*. (4) The elements which are the most widely distributed in nature have *small* atomic weights, and all the elements of small atomic weight are characterised by sharply defined properties. They are therefore typical elements. (5) The *magnitude* of the atomic weight determines the character of an element. (6) The discovery of many yet unknown elements may be expected. For instance, elements analogous to aluminium and silicon, whose atomic weights would be between 65 and 75. (7) The atomic weight of an element may sometimes be corrected by the aid of a knowledge of those of the adjacent elements. Thus the combining weight of tellurium must lie between 123 and 126, and cannot be 128. (8) Certain characteristic properties of the elements can be foretold from their atomic weights.

The entire periodic law is included in these lines. In the series of subsequent papers (1870-72, for example, in the *Transactions* of the Russian Chemical Society, of the Moscow Meeting of Naturalists, of the St. Petersburg Academy, and Liebig's *Annalen*) on the same subject we only find applications of the same principles, which were afterwards confirmed by the labours of Roscoe, Carnelley, Thorpe, and others in England; of Ramsdell (cerium and uranium), L. Meyer (the specific volumes of the elements), Zimmermann (uranium), and more especially of C. Winkler (who discovered germanium, and showed its identity with ekasilicon), and others in Germany; of Lecoq de Boisbaudran in France (the discoverer of gallium=ekaluminium); of Clève (the atomic weights of the cerium metals), Nilson (discoverer of scandium=ekaboron), and Nilson and Pettersson (determination of the vapour density of beryllium chloride) in Sweden; and of Brauner (who investigated cerium, and determined the combining weight of tellurium=125) in Austria, and Piccini in Italy.

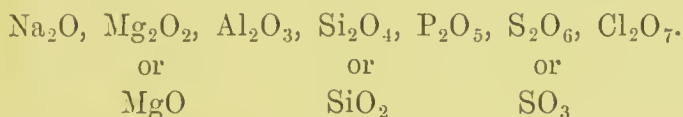
I consider it necessary to state that, in arranging the periodic system of the elements, I made use of the previous researches of Dumas, Gladstone, Pettenkofer, Kremers, and Lenssen on the atomic weights of related elements, but I was not acquainted with the works preceding mine of De Chancourtois (*vis tellurique*, or the spiral of the elements according to their properties and equivalents) in France, and of J. Newlands (Law of Octaves—for instance, H, F, Cl, Co, Br, Pd, I, Pt form the first octave, and O, S, Fe, Se, Rh, Te, Au, Th the last) in England, although certain germs of the periodic law are to be seen in these works. With regard to the work of Prof. Lothar Meyer respecting the periodic law (notes 12 and 13), it is evident, judging from the method of investigation and from his statement (Liebig's *Annalen*, *Supt. Band* 7, 1870, 354), at the very commencement of which he cites my paper of 1869 above mentioned, that he accepted the periodic law in the form which I proposed.

In concluding this historical statement I consider it well to observe that no law of nature, however general, has been established all at once; its recognition is always preceded by many presentiments; the establishment of a law, however, does not take place when the first thought of it takes form, or even when its significance is recognised, but

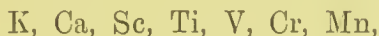
from 1 for hydrogen to 239 for uranium,^{8a} given at the beginning of this book, is arranged in conformity with this law. This arrangement of the elements immediately shows that starting from the alkali metals, Li, Na, K, Rb, and Cs, the power of the elements to combine with oxygen at first increases uniformly with the atomic weight; for instance, in the series



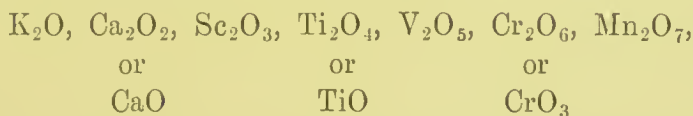
the atomic weight gradually increases from 23 to 35.5, and the higher oxides are:



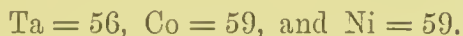
When the element of group VII., giving R_2O_7 , is reached, then either a new similar series begins after the element of the argon group (Chap. V.), so that, for example, after Cl and the argon series, we have:



which again give the same types of oxides:



or else the elements of group VII. continue as in the above instance, after $\text{Mn} = 55$ coming:



The most important points to be noticed here are that, as the atomic weight increases, (1) the series of the elements of a **small period** of seven groups from I. = R_2O to VII. = R_2O_7 periodically repeats itself,

only when it has been confirmed by the results of experiment, which the man of science must consider as the only proof of the correctness of his conjectures and opinions. I therefore, for my part, look upon Roscoe, De Boisbaudran, Nilson, Winkler, Brauner, Carnelley, Thorpe, and others who verified the adaptability of the periodic law to chemical facts as the true founders of the periodic law, the further development of which still awaits many fresh workers.

^{8a} The atomic weights given in the tables at the beginning of this book have the values which follow from the theory of this subject explained in Chap. VII., and correspond with the sum of the existing (1902) data on this subject—assuming the atomic weight of oxygen to be conditionally 16. But in many portions of this book the fractions are neglected for the sake of brevity and simplicity; for instance, H is taken equal to 1 and not 1.008, Na = 23, and not 23.05, &c.; especially as, although these fractions have been confirmed for some of the elements (for instance, H, Na, N, Cl, &c.), they are not reliable for the majority. In such cases the atomic weights are given without fractions in the chief tables; for instance, Co = 59, I = 127.

and (2) a close resemblance exists between the properties of the elements of the large periods containing two small periods with the elements of group VIII. between the small periods and an element of the argon group at the end. As these last elements give no compounds, the group they form is known as the **zero group**^{8b} because those elements which give the higher oxides, R_2O , and consequently salts RX , form the 1st group; the elements giving R_2O_2 or RO as their highest degree of oxidation belong to the 2nd group; those giving R_2O_3 as their highest oxides form the 3rd group, and so on. The large periods (K, Rb, Cs) beginning with the alkali metals, which give the most powerful alkalis, end with the halogens which correspond to the most powerful acids and contain intermediate elements with less distinctly marked chemical properties. The elements having the lowest atomic weights, although they bear the general properties of a group, still show many peculiar and independent properties.⁹ Thus fluorine, as we saw, differs in many points from the other halogens, and lithium from the other alkali metals, and so on. These lightest elements may be termed

^{8b} When the periodic system was first established (1869) not only were argon and its analogues, and their incapacity to enter into any of the ordinary forms of combination, unknown, but there were no reasons for even suspecting the existence of such elements. Now that the entire group, He, Ne, Ar, Kr, and Xe, is known, and also the fact that they evidently have as much in common as the group of the alkali metals or halogens, it must be admitted that they are as closely united together as either of these groups. This formed a sort of trial test for the theoretical side of the periodic law, like that put to it when beryllium was placed among the elements of group II. and not of group III. And as this test was successfully borne (for the oxide of beryllium corresponds in composition to the oxides of group II., as it should do, according to the law), so also the periodicity of the elements is in no way destroyed, but rather satisfied, by the argon elements, as explained in Chap. V., note 64. These elements, as Ramsay showed by their atomic weights in 1900, occupy a definite position between the halogens and alkali metals. They form their peculiar **zero group**, as explained in Chap. V., note 64. The necessity for a zero group was first recognised by Errera in Belgium. I consider it well to add that, judging from the incapacity of the elements of this group to enter into combination, the analogues of argon should be placed before the elements of group I., and that, according to the spirit of the periodic system, they should have smaller atomic weights than the alkali metals. This proved to be actually the case, and therefore gave a brilliant confirmation of the truth of the principles of periodicity, and clearly showed the true position held by the analogues of argon among the elements already known. Hence we are enabled to develop these principles more broadly than previously, and to look for the discovery of the zero group with atomic weights far smaller than that of hydrogen. So we may assume that an element of the zero group having an atomic weight 0.4 (perhaps it is Young's coronium) stands in the first series before hydrogen, and a limiting element with an infinitely small atomic weight, incapacity for chemical reaction, and exceedingly rapid motion of its (gaseous) molecules in the zero series of the zero group. Perhaps these properties should be ascribed to the atoms of universal all-penetrating ether. This idea is mentioned in the Preface of this book and also in a special article.

⁹ This resembles the fact, well known to those having an acquaintance with organic chemistry, that in a series of homologues (Chap. VIII.) the first member (for instance, CH_4 , CH_3O , CH_2O_2 , &c.), in which there is the least carbon, although showing the general properties of the homologous series, presents also certain distinct peculiarities.

typical elements. They include, besides hydrogen (1st series), the 2nd and 3rd series; the 2nd begins with He and Li, the 3rd with Ne and Na, and they end with F and Cl. Thus, the alkali metals stand first here, as in the large periods, and the halogens at the end, which shows that these elements form special **small periods**:

H.

Li, Be, B, C, N, O, F.

Na, Mg . . .

In the annexed table all the remaining elements (excepting those rare elements—for instance, Pr, Nd, Sm, &c.—which have not yet been fully investigated, and the analogues of argon) are arranged according to *large periods*. In order to understand the essence of the matter, it must be remembered that here the atomic weight gradually increases along a given line; for instance, in the line commencing with K = 39 and ending with Br = 80, the intermediate elements have intermediate atomic weights, as is clearly seen in the tables given in the Preface, where the elements stand in the order of their atomic weights.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.			I.	II.	III.	IV.	V.	VI.	VII.
Even Series.																
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
Rb	Sr	Y	Zr	Nb	Mo	—	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I
Cs	Ba	La	Ce	—	—	—	—	—	—	—	—	—	—	—	—	—
—	—	Yb	—	Ta	W	—	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	—	—
—	—	—	Th	—	U	<div style="text-align: center;"> Uneven Series. </div>										

In making use of the periodic system it is also useful to distinguish the *even* and *uneven* series in the large periods. The even series, beginning with the argon and alkali elements, gradually pass to the metals of group VIII., which are followed by the elements of the uneven series, ending with the true halogens, Cl, Br, I. In this manner the periodic system of the elements is fully expressed by arranging them in periods, series, and groups, as shown in the two tables given in the Preface of this book, which has been written entirely under the influence of the periodic system.

The same degree of analogy that we know to exist between potassium, rubidium, and caesium; or chlorine, bromine, and iodine; or calcium, strontium, and barium, also exists between the elements of the other vertical columns. Thus, for example, zinc, cadmium, and mercury, which are described in the following chapter, present a very close analogy with magnesium.^{9a}

^{9a} A certain decrease in the number of analogues is observed in passing from group I. to group VIII. There are five analogues (H, Na, Cu, Ag, Au) in the uneven

For a true comprehension of the matter¹⁰ it is very important to see that all the aspects of the distribution of the elements according to the

series of group I., four (Mg, Zn, Cd, Hg), in the same series of II., also four in groups III., IV., and V., but only three (S, Se, Te) in group VI., and the same number in groups VII. and VIII. Almost the same decrease is observed in the number of analogues of the even series. If an exceedingly light element (note 86) be recognised in the even series of the zero group, besides He, Ar, Kr, Xe, and Ne, this will also include five analogues; but the uneven series will only have two in the 1st and 3rd series. It is evident that of the typical elements of the small periods among the corresponding elements of the large periods only seven elements can be expected in the zero group, six (H, Li, Na, K, Rb, Cs) in group I., and less and less in the following groups; for instance, four in group VI. (O, S, Se, and Te) and only three in group VIII.

¹⁰ Besides arranging the elements (a) in a successive order according to their atomic weights, with indication of their analogies by showing some of the properties—for instance, their power of giving one or another form of combination—both of the *elements* and of their compounds (as is done in the table at the end of Chap. XV. and in the Preface), (b) according to periods (as after the Preface), and (c) according to groups and series or small periods (as in the same tables), I am acquainted with the following methods of expressing the periodic relations of the elements: (1) *By a curve* drawn through points obtained in the following manner: The elements are arranged along the horizontal axis as abscissæ at distances from zero proportional to their atomic weights, whilst the values for all the elements of some property—for example, the specific volumes or the melting-points, are expressed by the ordinates. This method, although graphic, has the theoretical disadvantage that it does not in any way indicate the existence of a limited and definite number of elements in each period. There is nothing, for instance, in this method of expressing the law of periodicity to show that between magnesium and aluminium there can be no other element with an atomic weight of, say, 25, atomic volume 13, and in general having properties intermediate between those of these two elements. The actual periodic law does not correspond with a continuous change of properties, with a continuous variation of atomic weight—in a word, it does not express an uninterrupted function—and as the law is purely chemical, being based upon the conception of atoms and molecules which combine in multiple proportions, i.e., with intervals (not in all proportions), it depends *above all* on there being but few types of compounds which are arithmetically simple, *repeat themselves* and offer no uninterrupted transitions, so that each period can only contain a definite number of members. For this reason there can be no other elements between magnesium, which gives MgX_2 , and aluminium, which forms AlX_3 ; there is a break in the continuity, according to the law of multiple proportions. The periodic law ought not, therefore, to be expressed by geometrical lines in which continuity is always understood, but rather in the manner of the theory of numbers—intermittently. Owing to these considerations I never have and never shall express the periodic relations of the elements by any geometrical figures. (2) *By a plane spiral*. Radii are traced from a centre, proportional to the atomic weights; analogous elements lie along one radius, and the points of intersection are arranged in a spiral. This method, adopted by De Chancourtois, Baumhauer, E. Huth, H. Erdmann, and others, has many of the imperfections of the preceding, although it removes the indefiniteness as to the number of elements in a period. It is merely an attempt to reduce the complex relations to a simple graphic representation, since the equation to the spiral and the number of radii are not dependent upon anything. (3) *By the lines of atomicity*, either parallel, as in Reynolds's and the Rev. S. Haughton's methods, or as in Crookes's method, arranged to the right and left of an axis, along which the magnitudes of the atomic weights are counted, and the position of the elements marked off, on the one side the members of the even series (para-magnetic, like oxygen, potassium, iron), and on the other side the members of the uneven series (diamagnetic, like sulphur, chlorine, zinc, and mercury). On joining up these points a periodic curve is obtained, compared by Crookes to the oscillations of a pendulum, and

order of their atomic weights express essentially one and the same

according to Haughton, representing a cubical curve. This method would be very graphic did it not require, for instance, that sulphur should be considered as bivalent and manganese as univalent, although neither of these elements gives stable derivatives of these types, and although the one is taken on the basis of the lowest possible compound SX_2 , and the other on that of the highest, because manganese can be referred to the univalent elements only by the analogy of $KMnO_4$ to $KClO_4$. Furthermore, Reynolds and Crookes place hydrogen, iron, nickel, cobalt, and others outside the axis of atomicity, and consider uranium as bivalent without the least foundation. (4) Rantsheff endeavoured to classify the elements in their periodic relations by a system dependent on solid geometry. He communicated this mode of expression to the Russian Chemical Society, but his communication, which is apparently not void of interest, has not yet appeared in print. (5) *By algebraic formulæ*: for example, E. J. Mills (1886) endeavours to express all the atomic weights by the logarithmic function, $A = 15(n - 0.9375t)$, in which the variables n and t are whole numbers. For instance, for oxygen $n = 2$ and $t = 1$, so that $A = 15.94$; for antimony $n = 9$, $t = 0$, whence $A = 120$, and so on. n varies from 1 to 16, and t from 0 to 59. The analogues are hardly distinguishable by this method: thus for chlorine the magnitudes of n and t are 3 and 7, and for bromine, 6 and 6; for iodine 9 and 9; for potassium 3 and 14; for rubidium 6 and 18; for caesium 9 and 20; but a certain regularity seems to be shown. One of the best attempts in this direction was made by J. H. Vincent (1902), who expressed the atomic weight, W , by the equation, $W = N^{1.21}$, where N is a series of whole numbers from $N = 1$ for hydrogen to $N = 92$ for uranium. The periodicity is almost lost sight of in this case. It is interesting, however, and has the advantage of clearly showing the existence between the atomic weights of breaks like those between whole numbers. The same refers to Mr. Schönrock's (Nijnii Novgorod, 1896) endeavour to find a harmonic or other function corresponding with the atomic weights and analogies of the elements. For instance, $A + 20 \log A = 3n + 34$ gives the atomic weight, A , for $C = 12.24$, if $n = 0$; $N = 14.05$, if $n = 1$; $O = 15.95$, if $n = 2$; $Mg = 24.29$, if $n = 6$, &c. (6) A more natural method of expressing the dependence of the properties of elements on their atomic weights is obtained by *trigonometrical functions*, because this dependence is periodic, and therefore Rydberg in Sweden (1885) and F. Flavitzky (Kazan, 1887) have adopted a similar method of expression, which must be considered worthy of being worked out, although it does not express the absence of intermediate elements; for instance, between magnesium and aluminium, which is essentially the most important part of the matter. (7) The investigations of B. N. Tchitchérin (1888) are an effort in the latter direction. This author only studied the alkali metals, and discovered the following relation between their atomic volumes: $v = A(2 - 0.0428An)$, where A is the atomic weight, and $n = 1$ for lithium and sodium, $\frac{1}{2}$ for potassium, $\frac{3}{8}$ for rubidium, and $\frac{5}{8}$ for caesium. This endeavour offers many interesting points, but it does not concern the atomic weight, and the starting-point of the theory is the specific gravity of the metals at a definite temperature, and the specific gravity varies even under mechanical influences. (8) L. Hugo (1884) endeavoured to represent the atomic weights of Li, Na, K, Rb, and Cs by geometrical figures; for instance, $Li = 7$ represents a central atom $= 1$ and six atoms on the six terminals of an octahedron; Na is obtained by applying two such atoms on each edge of an octahedron, and so on. Such methods can hardly add anything new to our data respecting the atomic weights of analogous elements. The above review shows that the tendency to represent graphically the periodicity of the elements and express the atomic weights by an exact function has not yet led to the desired result. It is, moreover, clear that the most promising are those efforts to express the variation of the atomic weights by functions, like those given in paragraph (5), which give breaks or jumps corresponding with the change in nature of the elements. In this respect Armstrong adopted the most direct method (1902) of expressing the atomic weights by a series of whole numbers without fractions; but his method leads to no consequences beyond what the periodic system has already given.

fundamental dependence—periodic properties.¹¹ The following points must then be remarked in it:—

¹¹ Many natural phenomena exhibit a dependence of a periodic character. Thus the phenomena of day and night and of the seasons of the year, and vibrations of all kinds, exhibit variations of a periodic character in dependence on time and space. But in ordinary periodic functions one variable varies continuously, whilst the other increases to a limit, then a period of decrease begins and in turn reaches its limit, after which a period of increase again begins. It is otherwise in the periodic function of the elements. Here the mass of the elements does not increase continuously, but abruptly, by steps, as from magnesium to aluminium. So also the valency or atomicity leaps directly from 1 to 2 to 3, &c., without intermediate quantities, and in my opinion it is these properties which are the most important, and it is their periodicity which forms the substance of the periodic law. It *expresses the properties of the real elements*, and not of what may be termed their manifestations visually known to us. The external properties of elements and compounds are in periodic dependence on the atomic weight of the elements only because these external properties are themselves the result of the properties of the real elements which unite to form the 'free' elements and the compounds. To explain and express the periodic law is to explain and express the causes of the law of multiple proportions and of the differences between the elements, and the variation of their atomicity, and at the same time to understand what mass and gravitation are. It is generally thought that this is still premature. But just as without knowing the cause of gravitation it is possible to make use of the law of gravity, so for the aims of chemistry it is possible to take advantage of the laws discovered by chemistry without being able to explain their causes. The above-mentioned peculiarity of the laws of chemistry respecting definite compounds and the atomic weights leads one to think that the time has not yet come for their full explanation, and I do not think that it will come before the explanation of such a primary law of nature as the law of gravity.

It will not be out of place here to turn our attention to the many-sided correlation existing between the **indecomposable elements and the compound carbon radicles**, which has long been remarked (Pettenkofer, Dumas, and others), and reconsidered in recent times by Carnelley (1886), and most originally in Pelopidas's work (1883) on the principles of the periodic system. Pelopidas compares the series containing eight hydrocarbon radicles, C_nH_{2n+1} , C_nH_{2n} , &c.; for instance, C_6H_{13} , C_6H_{12} , C_6H_{11} , C_6H_{10} , C_6H_9 , C_6H_8 , C_6H_7 , and C_6H_6 , with the series of the elements arranged in eight groups. The analogy is particularly clear owing to the property of C_nH_{2n+1} , to combine with X, thus reaching saturation, and of the following members with X_2 , X_3 , . . . X_8 , and especially because these are followed by an aromatic radicle— C_6H_5 —in which, as is well known, many of the properties of the saturated radicle C_6H_{13} , and in particular the power of forming a univalent compound, are repeated. Pelopidas shows a confirmation of the parallel in the property of the above radicles of giving oxygen compounds corresponding with the groups in the periodic system. Thus the hydrocarbon radicles of the first group—for instance, C_6H_{13} or C_6H_5 —give oxides of the form R_2O and hydroxides RHO , like the metals of the alkalis; and in the third group they form oxides R_2O_3 and hydrates RO_2H . For example, in the CH_3 series the corresponding compounds of the third group will be the oxide $(CH)_2O_3$ or $C_2H_2O_3$ —that is, formic anhydride and the hydrate, CHO_2H , or formic acid. In the sixth group, with a composition of C_2 , the oxide RO_3 will be C_2O_3 , and hydrate $C_2H_2O_4$ —that is, also a dibasic acid (oxalic) resembling, among the inorganic acids, sulphuric acid.

With respect to this remarkable parallelism, it must be observed that in the elements the atomic weight increases in passing to contiguous members of a higher valency, whilst here it decreases; but everything goes to prove that the periodic variability of elements and compounds is subject to some higher law whose nature, and cause, cannot at present be determined; and as the periodic law has only been generally recognised for a few years it is not surprising that any further progress towards its explanation can only be looked for in the development of facts touching on this subject.

1. The composition of the higher **oxygen compounds** is determined by the groups: the first group gives R_2O , the second R_2O_2 or RO , the third R_2O_3 , &c. There are eight types of oxides, and therefore eight groups. Two series give a large period, and the same type of oxide is met with twice in a large period. For example, in the period beginning with potassium, oxides of the composition RO are formed by calcium and zinc, and of the composition RO_3 by chromium, selenium, &c. The oxides of the even series, of the same type, have stronger basic properties than the oxides of the uneven series, and the latter as a rule are endowed with an acid character. Therefore the elements which give exclusively bases, like the alkali metals, will be found at the commencement of the period, whilst such purely acid elements as the halogens will be at the end of the period. It must be observed that the acid character is, in the main, peculiar to the elements with small atomic weights in the uneven series, whilst the basic character is exhibited by the heavier elements in the even series. Hence elements which give acids predominate chiefly among the lightest (typical) elements, and more especially in the last groups; whilst the heaviest elements, even in the last groups (for instance, thallium, uranium) have a basic character. Thus the basic and acid characters of the higher oxides are determined (*a*) by the type of oxide, (*b*) by the even or uneven series, and (*c*) by the atomic weight. The groups are indicated by Roman numerals from I. to VIII.

2. The **hydrogen compounds**, being volatile or gaseous substances which are prone to reaction—such as HCl , H_2O , H_3N , and H_4C ¹²—are only formed by the elements of the uneven series and higher groups giving oxides of the forms R_2O_7 , RO_3 , R_2O_5 , and RO_2 .

3. If an element gives a hydrogen compound, RX_m , it forms an **organo-metallic compound** of the same composition, where $X = C_nH_{2n+1}$, that is, the radicle of a saturated hydrocarbon. The elements of the uneven series, which are incapable of giving hydrogen compounds, and give oxides of the forms RX , RX_2 , RX_3 , also give organo-metallic compounds of this form proper to the higher oxides. Thus zinc forms the oxide ZnO , salts ZnX_2 , and zinc ethyl $Zn(C_2H_5)_2$. The elements of the even series (large periods) form organo-metallic compounds with difficulty.

¹² The hydrides generalised by the periodic law are those to which metallo-organic compounds correspond, and are themselves either volatile or gaseous. The hydrogen compounds, like Na_2H , BaH_2 , &c., are distinguished by other signs. They show (see end of last chapter) a systematic harmony, but they evidently should not be confused with true hydrides, any more than peroxides with saline oxides. Moreover, such hydrides have, like the peroxides, only recently been subjected to research, and have been but little studied.

4. The atomic weights of elements belonging to contiguous periods differ approximately by 45; for example, $K < Rb$, $Cr < Mo$, $Br < I$. But the elements of the typical series show much smaller differences. Thus the difference between the atomic weights of Li, Na, and K, between Ca, Mg, and Be, between Si and C, between S and O, and between Cl and F, is 16. As a rule, there is a greater difference between the atomic weights of two elements of one group and belonging to two neighbouring series ($Ti - Si = V - P = Cr - S = Mn - Cl = Nb - As$, &c. = 20); and this difference attains a maximum with the heaviest elements (for example, $Th - Pb = 26$, $Bi - Ta = 26$, $Ba - Cd = 25$, &c.). Thus even in the magnitude of the differences of the atomic weights of analogous elements there is observable a certain connection with the gradation of their properties.^{12a}

5. According to the periodic system every element occupies a certain position, determined by the group (indicated in Roman numerals) and series (Arabic numerals) in which it occurs. These indicate the atomic weight, the analogues, properties, and type of the higher oxide, and of the hydrogen and other compounds—in a word, all the chief quantitative and qualitative features of an element, although there yet remain a whole series of further details and peculiarities, the cause of which should perhaps be looked for in small differences of the atomic weights. If in a certain group there occur elements, R_1 , R_2 , R_3 , and if in that series which contains one of these elements, for instance R_2 , an element Q_2 precedes it and an element T_2 succeeds it, then the properties of R_2 are determined by the mean of the properties of R_1 , R_3 , Q_2 , and T_2 . Thus, for instance, the atomic weight of $R_2 = \frac{1}{4}(R_1 + R_3 + Q_2 + T_2)$. For example, selenium occurs in the same group as sulphur, $S = 32$, and tellurium, $Te = 127$, and, in the 7th series, $As = 75$ stands before it and $Br = 80$ after it. Hence the atomic weight of selenium should be $\frac{1}{4}(32 + 127 + 75 + 80) = 78.5$, which is near to that generally accepted, $Se = 79$, in which there is a possible error in the first decimal,

^{12a} The relation between the atomic weights, and especially the difference of 16, was observed in the sixth and seventh decades of the last century by Dumas, Pettenkofer, L. Meyer, and others. Thus Lothar Meyer in 1864, following Dumas and others, grouped together the tetravalent elements carbon and silicon; the trivalent elements nitrogen, phosphorus, arsenic, antimony, and bismuth; bivalent oxygen, sulphur, selenium, and tellurium; univalent fluorine, chlorine, bromine, and iodine, and the univalent metals lithium, sodium, potassium, rubidium, caesium, and thallium. The first germs of the periodic law are visible in such observations as these. Since its establishment this subject has been most fully worked out by Rydberg, who observed a periodicity in the variation of the differences between the atomic weights of two contiguous elements, and its relation to their atomicity (see Chap. XIV., note 9). A. Bazaroff (1887) investigated the same subject, taking, not the arithmetical differences of contiguous and analogous elements, but the ratio of their atomic weights; and he also observed that this ratio alternately rises and falls as the atomic weights increase.

so that 78·5 may be nearer the actual figure. Other properties of selenium may also be determined in this manner; for example, arsenic forms H_3As , bromine gives HBr , and it is evident that selenium, which stands between them, should form H_2Se , with properties intermediate between those of H_3As and HBr . Even the physical properties of selenium and its compounds, not to speak of their composition, being determined by the group in which it occurs, may be foreseen with a close approach to reality from the properties of sulphur, tellurium, arsenic, and bromine. **In this manner it is possible to foretell the properties of elements still unknown**, especially when it is surrounded by well-known elements. For instance, in the position, IV, 5—that is, in the IVth group and 5th series—an element is still wanting. These unknown elements may be named after the preceding known element of the same group by adding to the first syllable the prefix *eka-*, which means *one* in Sanskrit. The element IV, 5, follows after IV, 3, and this latter position being occupied by silicon, I named this formerly unknown element *ekasilicon* and its symbol Es . The following are the properties which this element should have on the basis of the known properties of silicon, tin, zinc, and arsenic. Its atomic weight is nearly 72, it forms a higher oxide EsO_2 , a lower oxide EsO , compounds of the general form EsX_4 , and chemically unstable lower compounds of the form EsX_2 . Es gives volatile organo-metallic compounds; for instance, $\text{Es}(\text{CH}_3)_4$, $\text{Es}(\text{CH}_3)_3\text{Cl}$, and $\text{Es}(\text{C}_2\text{H}_5)_4$, which boil at about 160° , &c.; also a volatile and liquid chloride, EsCl_4 , boiling at about 90° and of specific gravity about 1·9. EsO_2 will be the anhydride of a feeble colloidal acid, metallic Es will be rather easily obtainable from the oxides and from K_2EsF_6 by reduction, EsS_2 will resemble SnS_2 and SiS_2 , and will probably be soluble in ammonium sulphide; the specific gravity of Es will be about 5·5, and EsO_2 will have a density of about 4·7, &c. Such a prediction of the properties of *ekasilicon* was made by me in 1871, on the basis of the properties of the elements analogous to it; namely, IV, 3 = Si, IV, 7 = Sn, and also II, 5 = Zn and V, 5 = As. And now that this element has been discovered by C. Winkler, of Freiberg, Saxony, it has been found that its actual properties entirely correspond with those which were foretold, as was stated by Winkler in his excellent research on germanium.¹³ In this we see a most

¹³ The laws of nature admit of no exceptions, and in this they clearly differ from such rules and maxims as are found in grammar, and in other inventions, methods, and relations of man's creation. The confirmation of a law is only possible by deducing consequences from it, such as could not possibly be foreseen without it, and by verifying those consequences by experiment and further proofs. Therefore, when I perceived the periodic law, I (1869–1871, note 9) deduced such logical consequences from it as could serve to show whether it were true or not. Among them were the prediction of the

important confirmation of the truth of the periodic law. This element, now called germanium, Ge (see Chap. XVIII.), is not the only one that has been predicted by the periodic law.¹⁴ We shall see in describing the elements of the third group that properties were foretold of an element ekaaluminium, III, 5, $El = 68$, and were afterwards verified when the metal termed 'gallium' was discovered by Lecoq de Boisbaudran. So also, according to Nilson, the properties of scandium corresponded with those predicted for ekaboron.

6. As a true law of nature is one to which there are no exceptions, the periodic dependence of the properties on the atomic weights of the elements gives a **new means for determining** by the equivalent the **atomic weight** or atomicity of imperfectly investigated but known elements, for which no other means could as yet be applied for determining the true atomic weight. At the time (1869) when the periodic

properties of undiscovered elements and the correction of the atomic weights of many, at that time little known, elements. Thus uranium was considered as trivalent, $U = 120$; but as such it did not correspond with the periodic law. I therefore proposed to double its atomic weight— $U = 240$ —and the researches of Roscoe, Zimmermann, and others justified this alteration (Chap. XXI.). It was the same with cerium (Chap. XVIII.), whose atomic weight it was necessary to change according to the periodic law. I therefore determined its specific heat, and the result I obtained was verified by the new determinations of Hillebrand. I then corrected certain formulæ of the cerium compounds, and the researches of Rammelsberg, Brauner, Cleve, and others verified the proposed alterations. It was necessary to do one thing or the other—either to consider the periodic law as completely true, and as forming a new instrument in chemical research, or to refute it. Acknowledging the method of experiment to be the only true one, I myself verified what I could, and gave everyone the possibility of proving or confirming the law, and did not think, like L. Meyer (Liebig's *Annalen*, *Supt. Band* 7, 1870, 364), when writing about the periodic law, that 'it would be rash to change the accepted atomic weights on the basis of so uncertain a starting-point.' ('Es würde voreilig sein, auf so unsichere Anhaltspunkte hin eine Aenderung der bisher angenommenen Atomgewichte vorzunehmen.') In my opinion, the *basis* offered by the periodic law had to be verified or refuted, and experiment in every case verified it. The starting-point then became general. No law of nature can be established without such a method of testing it. Neither De Chancourtois, to whom the French ascribe the discovery of the periodic law, nor Newlands, who is put forward by the English, nor L. Meyer, who is now cited by many as its founder, ventured to foretell the *properties of undiscovered* elements, or to alter the 'accepted atomic weights,' or, in general, to regard the periodic law as a new, strictly established law of nature, as I did from the very beginning (1869).

¹⁴ When in 1871 I wrote a paper on the application of the periodic law to the determination of the properties of hitherto undiscovered elements, I did not think I should live to see the verification of this consequence of the law, but such was to be the case. Three elements were described—ekaboron, ekaaluminium, and ekasilicon—and now, after the lapse of twenty years, I have had the great pleasure of seeing them discovered and named Gallium, Scandium, and Germanium, after those three countries where the rare minerals containing them are found, and where they were discovered. For my part I regard L. de Boisbaudran, Nilson, and Winkler, who discovered these elements, as the true corroborators of the periodic law. Without them it would not have been accepted to the extent it now is. So also I consider that Prof. Ramsay has corroborated the periodic law by having discovered He, Ne, Ar, Kr, and Xe, and determined their atomic weights, which fully satisfy the requirements of the periodic system of the elements.

law was first proposed there were several such elements. It thus became possible to learn their true atomic weights, and these were verified by later researches. Among the elements thus concerned were indium, uranium, cerium, yttrium, and others.¹⁵

7. The periodic variability of the properties of the elements in dependence on their masses presents a distinction from other kinds of periodic dependence (as, for example, the sines of angles vary periodically and successively with the growth of the angles or the temperature of the atmosphere with the course of time—daily or yearly), in that the weights of the atoms do not increase gradually, but by leaps; that is, according to the laws of periodicity and multiple proportions (Dalton's), there not only are not, but there cannot be, any transition or intermediate elements between two neighbouring ones (for example, between $K=39$ and $Ca=40$, or $Al=27$ and $Si=28$, or $C=12$ and $N=14$, &c.). Just as in a molecule of a hydrogen compound there may be either one, as in HF , or two, as in H_2O , or three, as in NH_3 , &c., atoms of hydrogen to an atom of another element; but as there

¹⁵ Taking indium, which occurs together with zinc, as our example, we shall show the principle of the method employed. The equivalent of indium to hydrogen in its oxide is 37.7—that is, if we suppose its composition to be like that of water; then $In=37.7$, and the oxide of indium is In_2O . The atomic weight of indium was taken as double the equivalent—that is, indium was considered to be a bivalent element—and $In=2 \times 37.7=75.4$. If indium only formed an oxide, RO , it should be placed in group II. But in this case it appears that there would be no place for indium in the system of the elements, because the positions II., 5= $Zn=65$ and II., 6= $Sr=87$ were already occupied by known elements, and according to the periodic law an element with an atomic weight 75 could not be bivalent. As neither the vapour density nor the specific heat, nor even the isomorphism (the salts of indium crystallise with great difficulty) of the compounds of indium was known, there was no reason for considering it to be a bivalent metal, and therefore it might be regarded as trivalent, quadrivalent, &c. If it be trivalent, then $In=3 \times 37.7=113$, and the composition of the oxide is In_2O_3 and that of its salts InX_3 . In this case it at once falls into its place in the system, namely, in group III. and series 7, between $Cd=112$ and $Sn=118$, as an analogue of aluminium or dialuminium ($dvi=2$ in Sanskrit). All the properties observed in indium correspond with this position; for example, the density, cadmium=8.6, indium=7.4, tin=7.2; the basic properties of the oxides CdO , In_2O_3 , SnO_2 , vary regularly, so that the properties of In_2O_3 are intermediate between those of CdO and SnO_2 or Cd_2O_2 and Sn_2O_4 . That indium belongs to group III. has been confirmed by the determination of its specific heat (0.057 according to Bunsen, and 0.055 according to me) and also by the fact that, like aluminium, indium forms alums, and therefore belongs to the same group.

Similar considerations necessitated taking the atomic weight of titanium as nearly 48, and not as 52, the figure derived from many analyses. And these corrections, made on the basis of the law, have also been confirmed, for Thorpe found, by a series of careful experiments, the atomic weight of titanium to be that foreseen by the periodic law. Notwithstanding that previous analyses gave $Os=199.7$, $Ir=198$, and $Pt=187$, the periodic law shows, as I remarked in 1871, that the atomic weights should rise from osmium to platinum and gold, and not fall. Many researches, and especially those of Seubert, have fully verified this statement, based on the law. Thus a true law of nature anticipates facts, foretells magnitudes, gives a hold on nature, and leads to improvements in the methods of research, &c.

cannot be molecules containing $2\frac{1}{2}$ atoms of hydrogen to one atom of another element, so, according to the periodic law, there cannot be any element intermediate between N and O, with an atomic weight greater than 14 or less than 16, or between K and Ca. Hence the periodic dependence of the elements cannot be expressed by any continuous algebraical function in the same way that it is possible, for instance, to express the variation of the temperature during the course of a day or year.

8. The essence of the notions giving rise to the periodic law consists in a general physico-mechanical principle which recognises the correlation, transmutability, and equivalence of the forces of nature. Gravitation, attraction at small distances, and many other phenomena are in direct dependence on the mass of matter. It might therefore have been expected that chemical forces would also depend on mass. A dependence is in fact shown, the properties of elements and compounds being determined by the masses of the atoms of which they are formed. The weight of a molecule, or its mass, determines, as we have seen (Chap. VII. and elsewhere), many of its properties independently of its composition. Thus carbonic oxide, CO, and nitrogen, N₂, are two gases having the same molecular weight, and many of their properties (density, liquefaction, specific heat, &c.) are similar or nearly similar. The differences dependent on the nature of a substance play another part, and form magnitudes of another order. But *the properties of atoms are mainly determined by their mass* or weight, and are in dependence upon it.^{15a} As the mass increases the properties vary, at

^{15a} I have often been asked on what basis, and from what standpoint of thought, I discovered the periodic law which I defend so stubbornly. The following is the best answer I can give. Of the exact nature of matter we have no knowledge. The dynamic philosophers of old and some modern spiritualists who have meditated on this subject and have come to the conclusion that our conception of matter is entirely based upon impressions produced by phenomenal forces and forms of motion have either almost entirely denied the independent nature or existence of matter, or else have so far subjected it to the conception of force (energy) that they admit the creation of matter from force, although they do not recognise the reverse. Thought, which has no resting-place in the history of knowledge, is free to wander in these unlimited regions whither and how it pleases, and may therefore return to the point from which it started in the dawn of science. I do not in the least censure such thought in any respect, but when my thoughts turn to this region they always rest steadfastly on the fact that we are unable to comprehend matter, force, and the soul in their substance or reality, but are only able to study them in their manifestations in which they are inevitably united together, and that beyond their inherent indestructibility they also have their tangible, common, peculiar signs or properties which should be studied in every possible aspect. The results of my labours in the study of matter show me two such signs or properties in matter: (1) the *mass* which occupies space and evinces itself in gravity or more clearly and really in weight, and (2) the *individuality* expressed in chemical transmutations and most clearly formulated in the notion of the chemical elements. In thinking of matter outside any idea of material atoms, it is impossible for me to exclude two

first successively and regularly, and then return to their original magnitude and commence a fresh period of variation like the first. Nevertheless, here as in other phenomena, there are cases in which a small variation of the mass of the atom leads to a small variation of properties, and determines differences of a second order. This is seen, for instance, in group VIII., which is treated more fully in Chapters XXII. and XXIII.; thus the atomic weights of cobalt and nickel, of rhodium, ruthenium, and palladium, and of osmium, iridium, and platinum, are very close to each other, and their properties are also very much alike, the differences being hardly perceptible. And if the properties of atoms are a function of their weight, many ideas which have more or less rooted themselves in chemistry must be developed and worked out in the sense of this deduction. Although at first sight it appears that the chemical elements are perfectly self-existent in their character, and completely independent of each other, yet this idea of the nature of the elements must now be replaced by the notion of the dependence of their properties upon *their mass*; that is to say, the subjection of the individuality of the elements to a common higher principle which evinces itself in gravity and in the majority of physico-chemical phenomena. Many chemical deductions then acquire a new sense and significance, and a regularity is observed where it would otherwise escape attention.

9. This is particularly apparent in the physical properties to the consideration of which we shall afterwards turn, and we will now point out that first Gustavson (Chap. X., note 28) and subsequently Potilitzin (Chap. XI., note 66) demonstrated the dependence of purely reactive powers on the atomic weight and on that fundamental property which is expressed in the forms of their compounds, whilst in a number of other cases the purely chemical relations of elements proved to be in connection with their periodic properties. As a case in point, it may be

questions: How much and what kind of matter? Which qualities correspond to the conceptions of mass and of the chemical elements? And the history of the science of matter, that is, of chemistry, inevitably compels us to recognise the indestructibility not only of matter but also of the chemical elements. Therefore the thought involuntarily arises that there must be some bond of union between mass and the chemical elements; and as the mass of a substance is ultimately expressed (although not absolutely, but only relatively) in the atom, a functional dependence should exist and be discoverable between the individual properties of the elements and their atomic weights. But nothing, from mushrooms to a scientific dependence, can be discovered without looking and trying. So I began to look about and write down the elements with their atomic weights and typical properties, analogous elements, and like atomic weights on separate cards, and this soon convinced me that the properties of the elements are in periodic dependence upon their atomic weights; and although I have had my doubts about some obscure points, yet I have never once doubted the universality of this law, because it could not possibly be the result of chance.

mentioned that Carnelley remarked a dependence of the decomposability of the hydrates on the position of the elements in the periodic system; whilst L. Meyer, Willgerodt, and others established a connection between the atomic weight or the position of the elements in the periodic system and their property of serving as media in the transference of the halogens to the hydrocarbons.¹⁶ Bailey pointed out a periodicity in the stability (under the action of heat) of the oxides, namely: (a) in the even series (for instance, CrO_3 , MoO_3 , WO_3 , and UO_3) the higher oxides of a given group decompose with greater ease the smaller the atomic weight, whilst in the uneven series (for example, CO_2 , GeO_2 , SnO_2 , and PbO_2) the contrary is the case; and (b) the stability of the higher saline oxides in the even series (as in the fourth series from K_2O to Mn_2O_7) decreases in passing from the lower to the higher groups, while in the uneven series it increases from the group I. to IV. and then falls from IV. to VII.; for instance, in the series Ag_2O , CdO , In_2O_3 , SnO_2 , and then SnO_2 , Sb_2O_5 , TeO_3 , I_2O_7 . K. Winkler looked for and actually found (1890) a dependence between the reducibility of the metals by magnesium and their position in the periodic system of the elements, &c. The greater the attention paid to this field the more often is a distinct connection found between the variation of purely chemical properties of analogous substances and the variation of the atomic weights of the constituent elements and their position in the periodic system. Further, since the periodic system has become more firmly established, many facts have been gathered, showing that there are many similarities between Sn and Pb, B and Al, Cd and Hg, &c., which, although foreseen in some cases, had not been previously observed, and are a consequence of the periodic law. Keeping our attention in the same direction, we see that the most widely distributed elements in nature are those with small atomic weights; in organisms the lightest elements exclusively predominate (hydrogen, carbon, nitrogen, oxygen), the small mass of which facilitates those transformations peculiar to organisms. Poluta (of Kharkoff), C. C. Botkin, Blake, Brenton, and

¹⁶ Meyer, Willgerodt, and others, guided by the fact that Gustavson and Friedel had remarked that metalepsis proceeds rapidly in the presence of aluminium, investigated the action of nearly all the elements in this respect. For example, they took benzene, added to it the metals to be experimented on, and passed chlorine through the liquid in diffused light. When, for instance, sodium, potassium, barium, &c., are taken, there is no action on the benzene; that is, hydrochloric acid is not disengaged. But if aluminium, gold, or, in general, any metal having this power of aiding chlorination (*Halogen-überträger*) is employed, the action is then clearly seen from the volumes of hydrochloric acid evolved (especially if the metallic chloride formed is soluble in benzene). Thus, in group I., and in general among the even and light elements, there are none capable of serving as agents of metalepsis; but aluminium, gallium, indium, antimony, tellurium, and iodine, which are contiguous members in the periodic system, are excellent transmitters (carriers) of the halogens.

others even discovered a correlation between the physiological action of salts and other reagents on organisms and the positions occupied in the periodic system by the metals contained in them. Nobody thought of looking for such relations before the periodic law was established; a fact which proves it to be a natural and true law. A portion of the veil hiding the nature of the simple bodies has been to some extent raised by the periodic law.^{16a}

^{16a} The long-forgotten 'idea' of a primary matter from which all the simple bodies are supposed to have originated has been more and more frequently brought forward as the periodic law has taken root. This appears to me to be perfectly natural if mass be considered as directly dependent upon the quantity of a substance as is the case in mechanics. Before discussing this opinion—the composition of the atoms of simple bodies from the atoms of primary matter—I think it necessary to draw attention to the fact that the conception of mass is derived exclusively from gravity or weight, that is, from the action of forces and the study of motions. At the present day we have every right to say that different forces act on a substance in conformity with the action of gravity on it, but nothing tells us that we therefore (from the weight) know the quantity of matter in the substance; for Newton and Bessel's experiments, which showed that pendulums of equal lengths and equal weights vibrate in equal periods of time, although they be of different material (and also the similar experiments with horizontal 'torsion' pendulums), only prove that the action of the forces in the weighings and vibrations of the pendulums are equal and almost similar in all respects, but they do not explain the conception of the quantity of matter; this remains a conditional silent compromise recognising that the weight or mass is proportional to the quantity of matter, or else, according to the notion of a primary form of matter, proportional to the number of atoms of this primary matter. For my part I have not the slightest wish to unsettle the fruitful doctrine of mass, but only desire to point out that if chemical doctrines had been developed before physico-mechanical ones, the atomic quantities of simple bodies might have been regarded as perfectly independent in their nature, and as acting according to their weight in all their chemical and also physico-mechanical relations, that is, that masses which are similar in a mechanical sense do not contain similar quantities of a substance, while masses with a similar amount of a substance, that is, with a similar number of different atoms, do not act similarly in a physico-mechanical sense (i.e., at certain distances), but according, and in proportion, to their inherent peculiarities, which are retained both when the atoms form simple bodies and when they enter into different combinations. By this I only wish to say that for me the conceptions of the chemical elements and what (beyond any atomic theory) we consider as their atomic weights belong to those primary conceptions of all natural science, like those of mass or quantity of matter, and I think that in the future when chemistry shall have reached the age of mechanics (there is a difference of almost two centuries, and the more youthful chemistry is growing more rapidly than mechanics), some kind of compromise will be arrived at, and the quantity of a substance will be calculated in a manner quite different from the present one, although the conceptions of mass and atomic weight will be retained.

It was necessary that I should give the above general considerations in order to explain my personal views on the question of the formation of the simple bodies from a supposed primary form of matter. I cannot refute it, but it is still more impossible for me to accept it, for there are at the present day no sound bases for supporting such a view. And as experiment so far denies the possibility of transmuting the elements into each other, and in no wise explains the chemical nature of the ether and its transition into matter, it appears to me that the whole question of a primary matter belongs to the province of fancy and not of science, and I do not recommend any beginning to study chemistry—and this book is designed for such—to occupy themselves with it.

10. When (1869–1871) the periodic law was first established, such very inactive elements, in a chemical sense, as the analogues of argon (He, Ne, Kr, and Xe) were utterly unknown and could not be foreseen. Hence the position they occupied among the other elements offered a most important means for strengthening the conceptions of this law. And indeed, judging from the fact that the argon elements do not enter into combination, they should, according to the periodic law, be placed in a zero group, that is, before group I., and they should therefore have smaller atomic weights than the elements of this group (see Chap. V., note 64).

11. As, from the necessity of the case, the physical properties of the elements and compounds must be in dependence on the composition of a substance, i.e., on the quality and quantity of the elements forming it, so for them also must be expected a dependence on the atomic weight of the component elements, and consequently also on their periodic distribution.¹⁷ We shall meet with repeated proofs of this in the further exposition of our treatise, and for the present will content ourselves with citing the discovery by Errera (Belgium) in 1878 and by Carnelley in 1879 of the dependence of the magnetic properties of the elements on the position occupied by them in the periodic system. They showed that all the elements of the *even series* (beginning with lithium, potassium, rubidium, cæsium) belong to the class of *magnetic* (paramagnetic) substances; for example, according to Faraday and others,^{17a} C, O, Mg, Al, Si, Ti, V, Cr, Mn, Fe, Co, Ni, Y, Nb, Mo, Ru, Rh, Pd, Ba, La, Ce, W, Os, Ir, Pt, Th, U, are magnetic; and the elements of the *uneven series* are *diamagnetic*, H, Na, P, S, Cl, Cu, Zn, Se, Br, Ag, Cd, Sb, Te, I, Au, Hg, Tl, Pb, Bi. Carnelley also showed that the **melting-point** of elements varies periodically, as is seen by the figures

¹⁷ The periodic relations enumerated above appertain to the real elements, and not to the elements in the free state as we know them; and it is very important to note this, because the periodic law refers to the real elements, inasmuch as the atomic weight is proper to the real element, and not to the 'free' element, to which, as to a compound, a molecular weight is proper. Physical properties are chiefly determined by the properties of molecules, and only indirectly depend on the properties of the atoms forming the molecules. For this reason the periods, which are clearly and quite distinctly expressed—for instance, in the forms of combination—become to some extent involved (complicated) in the physical properties of their members. Thus, for instance, besides the *maxima* and *minima* corresponding with the periods and groups, new molecules appear; for example, as regards the melting-point of germanium, a local *maximum* appears, which was, however, foreseen by the periodic law when the properties of germanium (ekasilicon) were forecast.

^{17a} The relation of certain elements (for instance, the analogues of Pt) among diamagnetic and paramagnetic bodies is sometimes doubtful (probably owing partly to the imperfect purity of the reagents under investigation). This subject was studied in some detail by Bachmetieff in 1889.

in the accompanying table (last column) ¹⁸ where all the most trustworthy data are collected, predominance being given to those having maximum and minimum values. ¹⁹

¹⁸ It is evident that many of the temperatures, especially those exceeding 1000°, have been determined with but little exactitude, and some, placed in the accompanying table with the sign (?), I have only given on the basis of rough and comparative determinations, calculated from the melting-points of silver and platinum, now established by many observers. Judging by this table, besides the large periods whose maxima correspond with carbon, silicon, vanadium, manganese, and osmium, there are also small periods in the melting-points, and their maxima correspond with Ge, Te. The minima correspond with the halogens and metals of the alkalis. A distinct periodicity is also seen in the coefficients of linear expansion (chiefly according to Fizeau); for instance, in the vertical series (according to the magnitude of the atomic weight), Fe, Co, Ni, Cu, the linear expansions in millionths of an inch are 12, 13, 17, and 29; for Rh, Pd, Ag, Cd, In, Sn, and Sb the coefficients are 8, 12, 19, 31, 46, 26, and 12, so that a maximum is reached at In. In the series Ir (7), Pt (5), Au (14), Hg (60), Tl (31), Pb (29), and Bi (14), the maximum is at Hg and the minimum at Pt. Raoul Pictet expressed this connection by the product $\alpha(t+273) \sqrt[3]{A/d}$, which he found to be nearly constant for all elements in the free state, and equal to about 0.045, α being the coefficient of linear expansion, $t+273$, the melting-point calculated from the absolute zero (-273°), and $\sqrt[3]{A/d}$, the mean distance between the atoms, if A is the atomic weight and d the sp. gr. of an element. Although the above product is not strictly constant, nevertheless Pictet's rule gives an idea of the bond between magnitudes which ought to have a certain connection with each other. De Heen, Nadeschdin, and others also studied this dependence, but their deductions do not give a general and exact law. Further details must be sought in works on physical chemistry. But I think it necessary to add that many often seek for physical properties a dependence upon the specific volumes, and this dependence may always be transferred to one upon the atomic weights, because the specific volumes are themselves functions of the atomic weights.

¹⁹ Carnelley found a similar dependence on comparing the melting-points of the metallic chlorides, many of which he redetermined for this purpose. The melting-points (and boiling-points, in brackets) of the following chlorides are known, and a certain regularity is seen to exist in them, although the number (and degree of accuracy) of the data is insufficient for a generalisation:—

LiCl 598°	BeCl ₂ 600°	BCl ₃ -20°
NaCl 772°	MgCl ₂ 708°	AlCl ₃ 187°
KCl 734°	CaCl ₂ 719°	ScCl ₃ ?
CuCl 484° (993°)	ZnCl ₂ 262° (680°)	GaCl ₃ 76° (217°)
AgCl 451°	CdCl ₂ 541°	InCl ₃ ?
TlCl 427° (713°)	PbCl ₂ 498° (908°)	BiCl ₃ 227°

Lauric (1882) also observed a periodicity in the **quantity of heat** developed in the formation of the chlorides, bromides, and iodides (fig. 89). This is seen from the following figures, which express the heat developed in thousands of calories, and referred to a molecule of chlorine, Cl₂, so that the heat of formation of KCl is doubled, and that of SnCl₄ halved, &c.: Na 195 (Ag 59, Au 12), Mg 151 (Zn 97, Cd 93, Hg 63), Al 117, Si 79 (Sn 64), K 211 (Li 187), Ca 170 (Sr 185, Ba 194). Hence the greatest amount of heat is evolved by the metals of the alkalis, and in each period the heat evolution falls from them to the halogens, which evolve very little heat in combining together. Richardson, by comparing the heats of formation of the fluorides, also came to the conclusion that they are in periodic dependence upon the atomic weights of the combined elements.

In this respect it may not be superfluous to remark: (1) that Thomsen, whose results

12. A. A. Baikoff (1902, a communication made to me), in his researches on many copper alloys, and guided by already existing data, came to the conclusion that copper follows the periodic system of the elements in its alloys of definite composition. That is, it behaves as an element of group I. like hydrogen. Thus its higher definite and characteristic alloys and compounds which contain the greatest proportion of copper have a composition MCu_2 with the elements of group II., belonging to the uneven series; MCu_3 for group III., MCu_4 for group

I have employed above, observed a correlation in the calorific equivalents of analogous elements, although he did not remark their periodic variation; (2) that the uniformity of many thermochemical deductions must gain considerably by the application of the periodic law, which evidently repeats itself in calorimetric data; and that these data frequently lead to true forecasts is due to the periodicity of the thermal as well as of many other properties, as was remarked by Laurie; and (3) that the heat of formation of

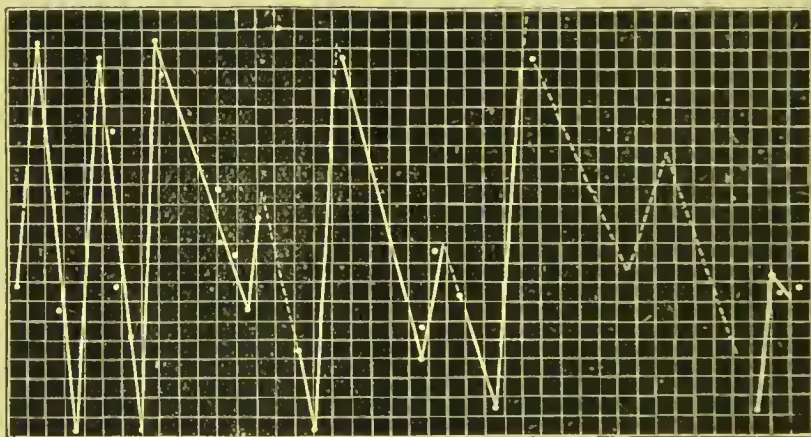


FIG. 89.—Laurie's diagram for expressing the periodic variation of the heat of formation of the chlorides. The abscissæ give the atomic weights from 0 to 210, and the ordinates the amounts of heat from 0 to 220 thousand calories evolved in the combination with Cl_2 (i.e., with 71 parts of chlorine). The apices of the curve correspond to Li, Na, K, Rb, Cs, and the lower extremities to F, Cl, Br, and I.

the oxides is also subject to a periodic dependence which differs from that of the heat of formation of the chlorides in that the greatest quantity corresponds with the bivalent metals of the alkaline earths (magnesium, calcium, strontium, barium), and not with the univalent metals of the alkalis, as is the case with chlorine, bromine, and iodine. This circumstance is probably connected with the fact that chlorine, bromine, and iodine are univalent elements, and oxygen bivalent (compare, for instance, Chap. XI., note 13, Chap. XXII., note 40, Chap. XXIV., note 28a, &c.).

Lecoq de Boisbandran, Rydberg, Ramage (Chap. XVII., note 27), Hartley, Keyser, and others, in investigating the spectra of the alkali metals and metals of the alkaline earths, &c., came to the conclusion that in this respect also there is a regularity of a periodic character in dependence upon the atomic weights. Probably a closer and systematic study of many of the properties of the elements and of complex and simple bodies formed by them will lead more and more frequently to similar conclusions, and to an extension of the range of application of the periodic law; such, for instance, as the refractive index, cohesion, ductility, and similar properties of corresponding compounds or of the elements themselves. Much has already been done in this respect, and details will be found in works on physical chemistry.

IV., MCu_3 for group V., MCu_2 for group VI., and MCu for VII. The following grouping of the most reliable cases explains this relation for the compounds of Cu, Ag, Na, and H:—

Group II. Cu_2Mg , Cu_2Zn , Cu_2Cd , Ag_2Zn , Ag_2Cd , Na_2Hg .

„ III. Cu_3Al .

„ IV. Cu_4Sn , H_4Si (and also Mg_2Sn , Al_4Sn_3).

„ V. Cu_3Sb , Ag_3Sb , Na_3Bi , H_3Sb .

„ VI. Cu_2S , Cu_2O , Ag_2O , H_2S .

„ VII. CuCl , CuI , HCl .

Thus the compositions of bronze ($\text{Cu} + \text{Sn}$), judging by the alloy Cu_4Sn , of brass ($\text{Cu} + \text{Zn}$), judging by the alloy Cu_2Zn , of aluminium bronze, judging by the alloy Cu_2Al and of the characteristic alloy Cu_3Sb , indicate a perfect analogy between the compounds of copper and chlorine Cl_4Sn , Cl_2Zn , Cl_3Al , and Cl_3Sb .^{19a} This is all the more remarkable because alloys in their analogy to solutions belong to the class of so-called indefinite compounds, in which many recognise the predominance of purely physico-mechanical agencies. It may be hoped that the application of the principle of periodicity noted by Baikoff will prove universal when different alloys have been carefully investigated in this light,^{19b} and that this method will give a new bond of a

^{19a} In a letter to me dated September 27, 1902, Mr. Baikoff concludes his remarks on the applicability of the periodic system to alloys, with the following words:—

‘The metallic compounds which correspond by the forms of their combination to the periodic law must be regarded as the most characteristic compounds. Thus with many combinations of metals forming several definite compounds, the relation between the higher (in Cu) form and the others is just like that between an anhydrous salt and its crystallohydrates. Examples of this kind are seen in the compounds SnCu_4 and SnCu_3 and SbCu_3 and SbCu_2 . Here the lower forms (SnCu_3 and SbCu_2) stand to their higher forms exactly like $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, for instance, which melts in its water of crystallisation with the separation of the anhydrous salt. It is, moreover, remarkable that the external properties of these lower forms are more characteristic than those of the higher forms; for instance, SbCu_2 is violet in colour. This also recalls what we see in salts, where we frequently meet with instances in which the most characteristic form is not the simplest fundamental, but the more complex, form, as is seen, for example, in the crystallohydrates, e.g., $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, &c. The dimorphism of the fundamental typical forms of the metallic compounds is characteristic. It is undoubted for SbCu_3 , SnCu_4 , Cu_2Zn , Cu_3Al , whilst the lower forms do not show this property. And with salts, dimorphism is far more frequent with the anhydrous salts, and is only comparatively rarely observed among crystallohydrates. All these relations indicate that the fundamental typical compounds of the metals are those which correspond to the periodic system, while the lower forms, although more stable under ordinary conditions, must be regarded as the result of combinations of the fundamental form with an excess of metal, just as crystallohydrates are formed by the union of water with the anhydrous salt.’

^{19b} The following short account of the alloys which have been most fully investigated up to the present day has the object of explaining in some measure what is said above concerning the alloys of copper. In this account I have availed myself of much that was communicated me by Mr. A. A. Baikoff.

The alloys of copper and tin, usually called bronzes, were first investigated by Rich, who recognised the formation of SnCu_3 and SnCu_4 among them. They were subsequently

most intimate nature uniting physico-mechanical relations with the general laws of chemistry. 13. There is no doubt that many other

studied by many others with somewhat divergent results. Some (Le Chatelier and Herschkowitsch) admit only one compound, SnCu_3 . This disparity is due to the fact that the fusing-point curves of the alloys have no maxima which would clearly indicate the composition of definite compounds, but show only 'critical' points. This is owing (Baikoff) to the facts: (1) that the compound SnCu_4 forms solid solutions with copper and (2) that the compound SnCu_3 decomposes in the act of fusion like salts containing water of crystallisation. The curve of fusion for the system $\text{Cu} + \text{Sn}$ was investigated with the greatest accuracy by Heycock and Neville. According to their data, there are two compounds, one having the composition SnCu_4 and containing exactly 32 per cent. of Sn and 68 per cent. of Cu, being indicated by a sharply defined bend in the curve for the alloy, the other, containing a larger proportion of tin, is also characterised by a 'critical' point, but its composition cannot be determined by the curve, as it decomposes in the act of fusion. This second compound is evidently SnCu_3 , the existence of which is proved by the electrical conductivity (Matthiessen) and electro-motive force (Laurie, Herschkowitsch), and which was separated as a crystalline powder by Le Chatelier from alloys rich in tin by the action of hydrochloric acid. Rich also showed that SnCu_3 and SnCu_4 are the only alloys of copper and tin which do not liquefy. Baikoff's observations on the fusing-points and micro-structure of these alloys showed that the alloy SnCu_4 solidifies completely at a constant temperature into a perfectly homogeneous alloy. All the alloys containing a greater proportion of tin and the alloy corresponding with the formula SnCu_4 show two pauses in solidifying, one break which is variable corresponding to the separation of crystals of SnCu_4 , and the other, which is constant, to the transition of SnCu_4 into SnCu_3 . This double fusing-point of SnCu_3 shows that this compound fuses with decomposition. The alloy SnCu_4 is dimorphous and passes from one crystalline form into another without in any way destroying the homogeneity of the alloy, although its structure is greatly modified by the changes. The dimorphism of the compound SnCu_4 explains the fact that bronze can be tempered. The alloy SnCu_4 is almost perfectly white, and is known as 'speculum metal,' as it is used for making mirrors and reflectors.

Alloys of copper and zinc are known as brasses. Researches on the fusing-points (Charpy), micro-structure (Charpy, Behrens, Le Chatelier), electro-motive force (Herschkowitsch), &c., indicate the existence of the compounds Cu_2Zn , CuZn , CuZn_2 (most easily recognised of all) and CuZn_4 . The truth of such conclusions is further confirmed by the fact that there is a whole series of chemical analogies. Thus, according to Heycock and Neville, the system $\text{Ag} + \text{Zn}$ comprises compounds Ag_2Zn , AgZn , and AgZn_2 ; the system $\text{Ag} + \text{Cd}$: Ag_2Cd , and, according to Baikoff, the system $\text{Cu} + \text{Cd}$ includes compounds Cu_2Cd and CuCd_2 . The alloys $\text{Cu} + \text{Mg}$ are found to give compounds Cu_2Mg and CuMg , but the compound CuMg_2 does not exist.

The alloys of copper and aluminium, according to the curve of fusion (Le Chatelier), comprise two compounds, AlCu_3 and Al_2Cu . The compound AlCu_3 corresponds to a maximum on the fusing-point curve, and may be separated from alloys rich in copper by the action of hydrochloric acid.

Copper and antimony, according to the researches of Baikoff, form two compounds, namely, SbCu_3 and SbCu_2 . The former corresponds to a maximum on the curve of fusion; it is greenish-white, and fuses without decomposition at 680° . It exists in two dimorphous forms, the point of transition of which lies at about 410°C . SbCu_3 forms solid solutions with copper and antimony, and the property of tempering, which these alloys exhibit to as great an extent as steel, is due to the formation and splitting up of these solutions. The sp. grs. of the two polymorphic modifications of the compound SbCu_3 are different, namely, 8.51 with rapid cooling, and 8.68 when cooled slowly. The compound SbCu_2 fuses with decomposition at 586°C , and is characterised by a critical point on the fusion curve; it has a beautiful violet colour. The existence of these two compounds is also revealed by the hardness, electro-motive force, coefficient of expansion, and micro-structure of the alloys of Cu and Sb.

physical properties will, when further studied, also prove to be in periodic dependence on the atomic weights (see note 19), but at present only a few are known with any completeness, and we will only refer to the one which is the most easily and frequently determined—namely, the **specific gravity** in the solid and liquid states, the more especially as its connection with the chemical properties and relations of substances is shown at every step. Thus, for instance, of all the metals those of the alkalis, and of all the non-metals the halogens, are the most energetic in their reactions, and they have lower specific gravities than the neighbouring elements, as is seen in the accompanying tables, pp. 46 and 47. Such are sodium, potassium, rubidium, caesium among the metals, and chlorine, bromine, and iodine among the non-metals; and as such less energetic metals as iridium, platinum, and gold (and even charcoal or the diamond) have higher specific gravities than the elements near to them in atomic weight, the degree of condensation of matter evidently influences the course of the transformations peculiar to a substance, and, furthermore, this dependence on the atomic weight, although very complex, is clearly of a periodic character. In order to account for this to some extent, it may be imagined that the lightest elements are porous, and, like a sponge, are easily penetrated by other substances, whilst the heavier elements are more compressed, and give way with difficulty to the insertion of other elements. These relations are best understood when, instead of the specific gravities referring to a unit of volume,²⁰ the **atomic volumes of the elements**—that is, the quotient A/d of the atomic weight A by the specific gravity d —are taken for comparison. As, according to the entire sense of the atomic theory, the actual matter of a substance does not fill up its whole cubical contents, but is surrounded by a medium (ethereal, as is generally imagined)—like the stars and planets which travel in the space of the heavens and fill it—with greater or less intervals, so the quotient A/d only expresses the *mean*

²⁰ Having occupied myself since the fifties (my dissertation for the degree of M.A. concerned the specific volumes, and is printed in part in the *Russian Mining Journal* for 1856) with the problems concerning the relations between the specific gravities and volumes and the chemical compositions of substances, I am inclined to think that the direct investigation of specific gravities gives essentially the same results as that of specific volumes, only that the latter are more graphic. Table III. of the periodic properties of the elements clearly illustrates this. Thus, for those members whose volume is the greatest among the contiguous elements, the specific gravity is least; that is, the periodic variation of both properties is equally evident. In passing, for instance, from silver to iodine we have a successive decrease of specific gravity and a successive increase of specific volume. The periodic alternation of the rise and fall of the specific gravity and specific volume of the free elements was communicated by me in August 1869 to the Moscow Meeting of Russian Naturalists. In the following year (1870) L. Meyer's paper appeared, which also dealt with the specific volumes of the elements.

volume corresponding to the sphere of the atoms, and therefore $\sqrt[3]{A/d}$ is the mean distance between the centres of the atoms. For compounds whose molecules weigh M , the mean magnitude of the atomic volume is obtained by dividing the mean molecular volume M/d by the number of atoms n in the molecule.²¹ The above relations may easily be expressed from this point of view by comparing the atomic volumes. Those comparatively light elements which enter easily and frequently into reaction have the greatest atomic volumes: sodium 23, potassium 45, rubidium 57, caesium 71, and the halogens about 27; whilst with those elements which enter into reaction with difficulty, the mean atomic volume is small; for carbon in the form of a diamond it is less than 4, and for charcoal about 6, for nickel and cobalt less than 7, for iridium and platinum about 9. The remaining elements having atomic weights and properties intermediate between those of the elements mentioned above have also intermediate atomic volumes. Therefore the specific gravities and specific volumes of solids and liquids stand in periodic dependence on the atomic weights, as is seen in the accompanying table, pp. 46 and 47, where both A (the atomic weight) and d (the specific gravity), and also A/d (specific volumes of the atoms) are given. Thus we find that in the large periods beginning with lithium, sodium, potassium, rubidium, caesium, and ending with fluorine, chlorine, bromine, iodine, the extreme members (energetic elements) have a small density and large volume, whilst the intermediate substances gradually increase in density and decrease in volume—that is, as the atomic weight increases the density rises and falls, again rises and falls, and so on. Furthermore, the energy decreases as the density rises, and the greatest density is proper to the atomically heaviest and least energetic elements, for example, Os, Ir, Pt, Au, U.

In order to explain the relation between the volumes of the elements and of their compounds, the densities (column S) and volumes (column M/S) of some of the higher saline oxides arranged in the same order as in the case of the elements are given on pp. 46 and 47. For convenience of comparison the volumes of the oxides are all calculated per two atoms of an element combined with oxygen. For example, the density of $Al_2O_3=4.0$; its weight, 102; and its volume, 25.5.

²¹ In my opinion the mean volume of the atoms of compounds deserves more attention than has yet been paid to it. I may point out, for instance, that for feebly energetic oxides the mean volume of the atom is generally nearly 7, for example, for the oxides SiO_2 , Se_2O_3 , TiO_2 , V_2O_5 , as well as ZnO , Ga_2O_3 , GeO_2 , ZrO_2 , In_2O_3 , SnO_2 , Sb_2O_3 , &c., whilst the mean volume of the atom of the alkali and acid oxides is greater than 7. Thus we find in the magnitudes of the mean volumes of the atom in oxides and salts both a periodic variation and a connection with their energy of essentially the same character as occurs in the case of the free elements.

Knowing the volume of aluminium to be 11, it is at once seen that in the formation of aluminium oxide, 22 volumes of it give 25.5 volumes of oxide, and therefore 3.5 volumes remain for O_3 , or only 1.2 volume per atom of oxygen. A certain periodicity may also be observed with respect to the specific gravities and volumes of the higher saline oxides. But it is especially important to call attention to the fact that the volume of the alkali oxides is less than that of the metal contained in them, which is also expressed in the last column, giving this difference for each atom of oxygen.²² Thus 2 atoms of sodium, or 46 volumes, give 24 volumes of Na_2O , and about 37 volumes of $2NaHO$; that is, the oxygen and hydrogen in distributing themselves in the medium of sodium have not only not increased the distance between its atoms, but have brought them nearer together, have drawn them together by the force of their great affinity, by reason, it may be presumed, of the small mutual attraction of the atoms of sodium. Such metals as aluminium and zinc, in combining with oxygen and forming oxides of feeble salt-forming capacity, hardly vary in volume; that is, only a small residue is left after subtracting the volume of the metal from that of the oxide; but the common metals and non-metals, and especially those forming acid oxides, always give an increased volume when oxidised; that is, the atoms are set further apart in order to make room for the oxygen. The oxygen in them does not compress the molecule as in the alkalis; it is therefore comparatively easily disengaged.

		M/S	Volume of Oxygen
H_2O 1.0	18	? — 22
Li_2O 2.0	15	— 9
Be_2O_2 3.06	16	+ 2.6
B_2O_3 1.8	39	+ 10.0
C_2O_1 1.6	55	+ 10.6
N_2O_5 1.64	66	? + 4
<hr/>			
Na_2O 2.6	24	— 22
Mg_2O_2 3.5	23	— 4.5
Al_2O_3 4.0	26	+ 1.2
Si_2O_1 2.65	45	+ 5.2

²² The volume of oxygen (judging by the table on this and the following pages) is evidently a variable quantity, forming a distinctly periodic function of the atomic weight and type of the oxide, and therefore the efforts which were formerly made to find the volume of the atom of oxygen in the volumes of its compounds may be considered to be futile. But since a distinct contraction always takes place in the formation of oxides, if the volume of an oxide is frequently less than the volume of the element combined with the oxygen, it might be surmised that the volume of oxygen in a free state is greater than its maximum calculated volume (11 for Ag_2O), and therefore about 12–15 (see note 24).

			S	M/S	Volume of Oxygen
P_2O_5	.	.	2.39	59	+ 6.2
S_2O_6	.	.	1.96	82	+ 8.7
Cl_2O_7	.	.	? 1.92	95	+ 6
<hr/>					
K_2O	.	.	2.7	35	— 35
Ca_2O_2	.	.	3.25	34	— 8
Sc_2O_3	.	.	3.86	35	? 0
Ti_2O_4	.	.	4.2	38	+ 3
V_2O_5	.	.	3.49	52	+ 6.7
Cr_2O_6	.	.	2.74	73	+ 9.5
Cu_2O	.	.	5.9	24	+ 9.6
Zn_2O_2	.	.	5.7	23	+ 4.8
Ga_2O_3	.	.	? 5.1	36	+ 4
Ge_2O_4	.	.	4.7	44	+ 4.5
As_2O_5	.	.	4.1	56	+ 6.0
<hr/>					
Sr_2O_2	.	.	4.7	44	— 13
Y_2O_3	.	.	5.0	45	? — 2
Zr_2O_4	.	.	5.5	44	0
Nb_2O_5	.	.	4.7	57	+ 6
Mo_2O_6	.	.	4.4	65	+ 6.8
Ag_2O	.	.	7.5	31	+ 11
Cd_2O_2	.	.	8.0	32	+ 3
In_2O_3	.	.	7.18	38	+ 2.7
Sn_2O_4	.	.	7.0	43	+ 2.7
Sb_2O_5	.	.	6.5	49	+ 2.6
Te_2O_6	.	.	5.1	68	+ 4.7
<hr/>					
Ba_2O_2	.	.	5.7	52	— 10
La_2O_3	.	.	6.5	50	+ 1
Ce_2O_4	.	.	6.74	50	+ 2
Ta_2O_5	.	.	7.5	59	+ 4.6
W_2O_6	.	.	6.8	68	+ 8.2
Hg_2O_2	.	.	11.1	39	+ 4.5
Pb_2O_4	.	.	8.9	53	+ 4.2
Th_2O_4	.	.	9.86	54	+ 2

As the volumes of the chlorides, the organo-metallic and all other corresponding compounds also vary in a like periodic succession with a change of elements, it is evidently possible to indicate the properties

of substances yet uninvestigated by experimental means, and even those of yet undiscovered elements. It was possible by following this method to foretell, on the basis of the periodic law, many of the properties of scandium, gallium, and germanium, which were verified with great accuracy after these metals had been discovered.²³ The periodic law, therefore, has not only embraced the mutual relations of the elements and expressed their analogy, but has also to a certain extent subjected to law the doctrine of the types of the compounds formed by the elements: it has enabled us to see a regularity in the variation of all chemical and physical properties of elements and compounds,²⁴ and

²³ As an example we will take indium oxide, In_2O_3 . Its sp. gr. and sp. vol. should be the mean of those of cadmium oxide, Cd_2O_3 , and stannic oxide, Sn_2O_4 , as indium stands between cadmium and tin. Thus in the seventies it was already evident that the volume of indium oxide should be about 38, and its sp. gr. about 7.2, which was confirmed by the determinations of Nilson and Pettersson (7.179) made in 1880.

²⁴ As the distance between, and the volumes of, the molecules and atoms of solids and liquids certainly enter into the data for the solution of the problems of molecular mechanics, which as yet have only been worked out to any extent for the gaseous state, the study of the specific gravity of solids, and especially of liquids, has long had an extensive literature. With respect to solids, however, a great difficulty is met with, owing to the specific gravity varying not only with a change of isomeric state (for example, for silica in the form of quartz it is 2.65, and in that of tridymite, 2.2), but also directly under mechanical pressure (for example, in a crystalline, cast, and forged metal), and even with the extent to which they are powdered, &c., which influences are imperceptible in liquids (compare Chap. XIV., note 55a).

Without going into further details, we may add to what has been said above that the conception of specific volumes and atomic distances has formed the subject of a large number of researches, but as yet it is only possible to lay down a few generalisations given by Dumas, Kopp, and others, which are mentioned and amplified by me in my work cited in note 20, and in my memoirs on this subject.

1. Analogous compounds and their isomorphs have frequently approximately the same molecular volumes.

2. Other compounds, analogous in their properties, exhibit molecular volumes which increase with the molecular weight.

3. When a contraction takes place in combination in a gaseous state, then, in the majority of instances, contraction is also to be observed in the solid or liquid state; that is, the sum of the volumes of the reacting substances is greater than the volume of the resultant substance or substances.

4. In decomposition the reverse of that which occurs in combination takes place.

5. In substitution (when the volumes in a state of vapour do not vary) a very small change of volume generally takes place; that is, the sum of the volumes of the reacting substances is almost equal to the sum for the resultant substances.

6 Hence it is impossible to judge of the volumes of the component substances from that of a compound, although it is possible to do so from the product of substitution.

7. The replacement of H_2 by sodium, Na_2 , and by barium, Ba , as well as the replacement of SO_4 by Cl_2 , scarcely changes the volume; but the volume increases with the replacement of Na by K , and decreases with the replacement of H_2 by Li_2 , Cu , and Mg .

8. There is no need for comparing volumes in a solid and a liquid state at the so-called corresponding temperatures; that is, at temperatures at which the vapour pressure is the same in each case. The comparison of volumes at the ordinary temperature is sufficient for finding a regularity in the relations of volumes (this deduction was developed by me in particular detail in 1856).

has rendered it possible to foretell the properties of elements and compounds yet uninvestigated by experimental means; thus it has prepared the ground for the building up of atomic and molecular mechanics.²⁵

9. Many investigators (Perseu, Schröder, Löwig, Playfair and Joule, Baudrimont, Einhardt) have sought in vain for a multiple proportion in the specific volumes of solids and liquids.

10. The truth of the above is seen very clearly in comparing the volumes of polymeric substances. The volumes of their molecules are equal in a state of vapour, but are very different in a solid and a liquid state, as is seen from the close resemblance of the specific gravities of polymeric substances. But as a rule the more complex polymerides are denser than the simpler.

11. We know that the hydroxides of light metals have generally a smaller volume than the metals, whilst that of magnesium hydroxide is considerably greater, which is explained by the stability of the former and the instability of the latter. In proof of this we may cite, besides the volumes of the true alkali metals, the volume of barium (36) which is greater than that of its stable hydroxide (sp. gr. 4.5, sp. vol. 30). The volumes of the salts of magnesium and calcium are greater than the volume of the metal, with the single exception of the fluoride of calcium. With the heavy metals the volume of the compound is always greater than the volume of the metal, and, moreover, for such compounds as silver iodide, AgI ($d=5.7$), and mercuric iodide, HgI₂ ($d=6.2$, and its volume, 73), the volume of the compound is greater than the sum of the volumes of the component elements. Thus the sum of the volumes Ag + I = 36, and the volume of AgI is 41. This stands out with particular clearness on comparing the volumes K + I = 71 with the volume of KI, which is equal to 54, its density being 3.06.

12. In such combinations, between solids and liquids, as solutions, alloys, isomorphous mixtures, and similar feeble chemical compounds, the sum of the volumes of the reacting substances is always very nearly that of the resulting substance, but here the volume is either slightly larger or smaller than the original; speaking generally, the amount of contraction depends on the force of affinity acting between the combining substances. I may here observe that the present data respecting the specific volumes of solid and liquid bodies deserve a fresh and full elaboration to explain many contradictory statements which have accumulated on this subject. As regards liquefied gases at their melting-points, I think it well to cite the following table given by Dewar (1900):—

Liquid	Sp. gr. at melting-point	Sp. vol.
Hydrogen	0.086	11.7
Nitrogen	1.10	13.1
Oxygen	1.27	12.6

The volume is naturally greater at the corresponding boiling-points, and at the absolute zero (-273°) the specific volumes approach 10-12; that is to say, they become almost equal.

²⁵ In demonstrating those aspects of the periodic law which speak most clearly in its favour, I consider it futile to discuss the numerous attacks which have been made on it, because they either throw no new light upon the law, or else have been refuted by further research. On the other hand I consider it necessary to mention three points concerning the periodic law which have not yet been reconciled with it, namely: (1) the atomic weights of cobalt and nickel, (2) the atomic weight of tellurium, and (3) the position of the so-called rare metals.

(1) Notwithstanding repeated and recent determinations of the atomic weights of Co and Ni, it is always found that, although these are very nearly equal, yet the atomic weight of Co is slightly larger than that of Ni, the value for Co being about 59.0 and that for Ni, 58.7; while, according to their analogy, and therefore according to the periodic

system, the atomic weight of Ni should be greater than that of Co, for they both stand between $\text{Fe}=55.9$ and $\text{Cu}=63.6$, and nickel approaches in all respects more nearly to Cu than to Fe, and Co more closely resembles Fe than Cu in its properties.

What is most wanted here are more new discriminative and *comparative* researches of great exactitude (such as the analysis of similar corresponding compounds of Ni and Co), for the results of different investigators cannot be said to be in perfect accord, and C. Winkler's researches even give the atomic weight of Ni as 59.4, which cannot, however, be the case. Moreover, nickel may be purified from the metals accompanying it in the form of a volatile compound $\text{Ni}(\text{CO})_4$, more perfectly than cobalt, and neither nickel nor cobalt offers such properties in its analogous compounds (oxides and salts) as could absolutely guarantee their being of strictly definite and constant composition. In a word there are many practical difficulties, and no chemist would, I think, deny that new researches might alter those decimals of the atomic weights which are in question. But even if the atomic weight of Ni eventually proves to be undoubtedly greater than Co, this would in no wise disturb the essence of the periodic law, especially as the question concerns the most uncertain group VIII., where the higher saline oxides are variable in composition and have no very distinctly marked properties. It is my personal opinion, however, that the atomic weight of Co most requires re-determining, and that it will prove less than that now accepted ($\text{Co}=59.0$) and less than that of Ni.

(2) Tellurium, in forming a higher saline oxide, TeO_3 , should certainly belong to group VI., and iodine, I, which gives HIO_4 and I_2O_7 , to group VII.; and yet Stas determined the generally adopted atomic weight $\text{I}=126.85$, and many recent determinations give Te =about 127.1, which is greater than that of iodine, although Brauner and others have frequently found the atomic weight of Te to be less than that of I. My own opinion has long been (since 1898, see vol. xxiii., *Encyclopædic Dictionary*, 'Periodic Law') that iodine should have an atomic weight greater than 126.85 and probably greater than 127, as mentioned in Chap. XI., note 62. In Ladenburg's recent (1902) determinations the iodine was dried over CaCl_2 , and it probably contained some chlorine (see also Chap. XX.).

(3) Among the so-called rare metals (Chap. XVII.) yttrium and cerium, the representatives of two special groups, found their position in the periodic system soon after the law was confirmed, and I determined the atomic weight of yttrium and also the specific heat of cerium with the object of seeing if the proposed modifications of their atomic weights (for yttrium from YO to Y_2O_3 , and for cerium from Ce_3O_4 to CeO_2) were permissible. All the subsequent researches of many chemists, and especially of Brauner, have confirmed the justice of my proposal, and the result has been extended not only to La and Di (this was done by me), but also to all the other rare metals whose oxides have since then been given the composition R_2O_3 , and scandium was found by Nilson to correspond to the looked-for ekaboron, $\text{Sc}=44.1$. The number of metals of this class subsequently became greater, and now those enumerated in Chap. XVII. are more or less known. A common composition, R_2O_3 , is given to the oxides (basic) of all these metals, on the strength of their analogy with the oxides R_2O_3 of yttrium, cerium, &c., which have found their proper position in the periodic system. There is no place in group III. of the periodic system for some of the rare metals with the type of oxide R_2O_3 , although there are two series of unoccupied places for elements with atomic weights 140–183, between $\text{Ce}=140$ and $\text{Ta}=183$. I have not formed any precise opinion on this score, and this appears to me to be one of the most difficult problems offered to the periodic law. However, the investigation of many of these metals is evidently insufficient to form a true opinion respecting the composition of their oxides, and in some cases even to be sure of their being independent elements, and I therefore think it premature to form a definite decision. At the Congress of Russian Naturalists in 1901, Prof. Brauner proposed placing all the rare metals about Ce, counting their atomic weights 140–183, in a special auxiliary group. I am not able to refute such a conclusion, but I think, however, that it would be more prudent to leave this question open, all the more so since $\text{Yb}=173$ (one of the best investigated of the rare metals) corresponds quite well, according to its atomic weight, to the position III., 10.

The higher hydrogen and organo-metallic compounds R = H, CH ₃ ...	The elements and their atomic weights.	The higher saline compounds X = $\frac{1}{2}$ O, (OH), Cl, (NO ₃), (OM), where M = K, $\frac{1}{2}$ Ca, $\frac{1}{3}$ Al, &c.	Simple bodies (elements).			
			Composition of the molecule.	Sp. gr. in solid and liquid states.	Sp. vol. in solid and liquid states.	Melting-point.
RH	H = 1.008		H ₂	0.08	max. 12	-256°
	He = 4.0		He			
RLi	Li = 7.03	LiX	Li	0.59	max. 12	+185°
R ₂ Be	Be = 9.1	BeX ₂	Be?	1.64	5.5	+950°
R ₃ B	B = 11.0	BX ₃	B _n	2.5	4.4 min.	+1300°?
R ₄ C	C = 12.0	CX ₄	C _n	1.9	6.3	+2700°?
R ₃ N	N = 14.04	NX . . . NX ₅	N ₂	1.1	13	215°
R ₂ O	O = 16.000	OX ₂	O ₂	1.27	12 min.	-250°
RF	F = 19.0	FX	F ₂	1.14	max. 17	-210°
	Ne = 19.9		Ne			-250°?
RNa	Na = 23.05	NaX	Na	0.98	max. 24	+97°
R ₂ Mg	Mg = 24.3	MgX ₂	Mg	1.74	14	700°
R ₃ Al	Al = 27.0	AlX ₃	Al	2.6	11 min.	657°
R ₄ Si	Si = 28.4	SiX ₄	Si _n	2.5	11 min. max.	1300°?
R ₃ P	P = 31.0	PX ₅	P ₄	2.2	14	+44°
R ₂ S	S = 32.06	SX ₆	S ₈	2.07	15	+114°
RCl	Cl = 35.45	ClX ClX ₇	Cl ₂	1.3	max. 27	-100°
	Ar = 38 ?		Ar			-190° min.
	K = 39.1	KX	K	0.87	max. 45	+60°
	Ca = 40.1	CaX ₂	Ca?	1.56	26	+800°
	Sc = 44.1	ScX ₃	Sc?	2.5?	18 ?	1200°?
	Ti = 48.1	TiX ₄	Ti?	3.6	13	2000°?
	V = 51.4	VX ₅	V?	5.5	9	max. 2500°?
	Cr = 52.1	CrX ₆	Cr?	6.7	7.7	1850°?
	Mn = 55.0	MnX ₂ . . . MnX ₇	Mn	7.5	7.3	1500°
	Fe = 55.9	FeX ₆	Fe	7.8	7.2	1450°
	Co = 59 ?	CoX ₄	Co	8.6	6.8	1400°
	Ni = 59 ?	NiX ₃	Ni	8.7	6.8 min.	1350°
			Cu	8.8	7.2	1054°
RCu	Cu = 63.6	CuX, CuX ₂	Zn	7.1	9.2	419°
R ₂ Zn	Zn = 65.4	ZnX ₂	Ga?	5.96	11.7	30° min.
R ₃ Ga	Ga = 70.0	GaX ₃	Ge	5.47	13.2	max. 900°
R ₄ Ge . . .	Ge = 72.3	GeX ₄	As ₄	5.65	13.3	500°
R ₃ As	As = 75.0	AsX ₅	Se ₆ ?	4.8	16	+217°
R ₂ Se	Se = 79 ?	SeX ₆	Br ₂	3.1	max. 26	-7
RBr	Br = 79.95	BrX BrX ₇	Kr			-100°? min.
	Kr = 81.8					
	Rb = 85.4	RX	Rb	1.5	max. 57	+39°
	Sr = 87.6	SrX ₂	Sr	2.5	35	600°?
	Y = 89.0	YX ₃	Y?	3.4	26	1000°?
	Zr = 90.6	ZrX ₄	Zr _n ?	4.1	22	1500°?
	Nb = 94	NbX ₅	Nb?	7.1	13	1700°?
	Mo = 96	MoX ₆	Mo?	8.6	11	max. 2200°?
	? = 99 ?	unknown ekamanganese.				
	Ru = 101.7	RuX ₂ . . . RuX ₈	Ru	12.2	8.3 min.	2000°?
	Rh = 103.0	RhX ₆	Rh	12.1	8.5	2000°?
	Pd = 106.5	PdX ₄	Pd	11.8	9.0	1800°
	Ag = 107.9	AgX	Ag	10.5	10.3	950°
R ₂ Cd	Cd = 112.4	CdX ₂	Cd	8.6	13	320°
R ₃ In	In = 114.0	InX ₃	In	7.4	14	176° min.
R ₄ Sn	Sn = 119.0	SnX ₄	Sn	7.2	16	232°
R ₃ Sb	Sb = 120	SbX ₅	Sb?	6.7	18	432°
R ₂ Te	Te = 127 ?	TeX ₆	Te?	6.4	20	455°
RI	I = 127 ?	IX IX ₇	I ₂	4.9	26	115°

The higher hydrogen and organo-metallic compounds R=H, CH ₃ ...	The elements and their atomic weights.	The highest saline compounds X = $\frac{1}{2}$ O, (OH), Cl, (NO ₂), (OM), where M = K, $\frac{1}{2}$ Ca, $\frac{1}{3}$ Al, &c.	Simple bodies (elements).				Melting-point.
			Composi- tion of the molecule.	Sp. gr. in solid and liquid states.		Sp. vol. in solid and liquid states.	
	Xe = 128						
	Cs = 132.9	CsX	Cs ?	2.4	max.	56	27° min.
	Ba = 137.4	BaX ₂	Ba ?	3.8		36	?
	La = 139	LaX ₃	La ?	6.1		23	?
	Ce = 140	CeX ₄	Ce	6.6		21	700° ?
	There is an unknown whole large period from Ce=140 to Ta=183. If the oxides be taken as R ₂ O ₃ , this period includes the rare metals Pr=140, Nd=144, Sm=150?, Gd=156, Tb=160, Er=166, Tu=171, and Yb=173.						
	Ta = 183	TaX ₅	Ta ?	10.4		18	?
	W = 184	WX ₆	W ?	19.1		9.6	2600°
	Unknown element: di-manganese? 188?						
	Os = 191	OsX ₃ . . . OsX ₈	Os ?	22.5	min.	8.5	max. 2700°
	Ir = 193	IrX ₆	Ir	22.4		8.6	2000°
	Pt = 194.9	PtX ₄	Pt	21.4		9.2	1775°
	Au = 197.2	AuX . AuX ₃	Au	19.3		10	+ 1045°
R ₂ Hg	Hg = 200.0	HgX ₂	Hg	13.6		15	- 39° min.
R ₁ Tl	Tl = 204.1	TlX ₃	Tl	11.8		17	+ 294°
R ₁ Pb	Pb = 206.9	PbX ₄	Pb	11.3		18	328°
R ₃ Bi	Bi = 208	BiX ₃ . . BiX ₅	Bi	9.8		21	269°
	Unknown elements with atomic weights from 208 to 232. Probably radium, Rd = 224, discovered by Madame Curie, belongs to this series.						
	Th = 232	ThX ₄	Th ?	11.1		21	1700° ?
	U = 239	UX ₆	U ?	18.7		13	

CHAPTER XVI

ZINC, CADMIUM, AND MERCURY

THESE three metals, like magnesium, give oxides RO , which form feebly energetic bases, and are also volatile. The volatility increases with the atomic weight. Magnesium can be distilled at a white heat, zinc at a temperature of about 930° , cadmium at about 770° , and mercury at about 357° . Their oxides, RO , are more easily reducible than magnesia, that of mercury being the most easily reducible. The properties of their salts RX_2 (solubility, power of forming double and basic salts, and many other qualities) are in many respects identical with those of MgX_2 . The difficulty with which they are oxidised, the instability of their compounds, the density of the metals and their compounds, their scarcity in nature, and many other properties increase gradually with the atomic weight. Their characteristics, as contrasted with those of magnesium, are to be expected from the fact that zinc, cadmium, and mercury are heavy metals.

Zinc stands nearest to magnesium in atomic weight and in many properties. Thus, for instance, zinc sulphate, or white vitriol, easily crystallises with seven molecules of water, $ZnSO_4 \cdot 7H_2O$. It is isomorphous with Epsom salts, and parts with difficulty with the last molecule of water; it forms double salts—for instance, $ZnK_2(SO_4)_2 \cdot 6H_2O$ —exactly as magnesium sulphate does.¹ Zinc oxide, ZnO , is a white powder, almost insoluble in water,² like magnesia, from which, how-

¹ Zinc sulphate is often obtained as a by-product—for instance, in the action of galvanic batteries containing zinc and sulphuric acid. When the anhydrous salt is heated it forms zinc oxide, sulphurous anhydride, and oxygen. The solubility in 100 parts of water at 0° is 43; at 20° , 53; at 40° , $63\frac{1}{2}$; at 60° , 74; at 80° , $84\frac{1}{2}$; and at 100° , 95 parts of anhydrous zinc sulphate—so that it is closely expressed by the formula, $43 + 0.52t$.

An admixture of iron is often found in ordinary sulphate of zinc in the form of ferrous sulphate, $FeSO_4$, isomorphous with the zinc sulphate. In order to separate this, chlorine is passed through the solution of the impure salt (when the ferrous salt is converted into ferric), the solution is then boiled and zinc oxide afterwards added, which, after some time has elapsed, precipitates all the ferric oxides. Ferric oxide, of the form R_2O_3 , is displaced by zinc oxide, of the form RO .

² Zinc oxide (flores zinci) is obtained by the combustion and oxidation of zinc, and by the ignition of some of its salts: for instance, those of carbonic and nitric acids; it is likewise precipitated by alkalis from a solution of ZnX_2 in the form of a gelatinous

ever, it is distinguished by its solubility in solutions of sodium and potassium hydroxides.³ Zinc chloride⁴ is decomposed by water,

hydroxide. The oxide produced by roasting zinc blende, ZnS (burning in the air, when the sulphur is converted into sulphurous anhydride), contains various impurities. For purification, the oxide is mixed with water, and the sulphurous anhydride formed by roasting the blende is passed through it. Zinc bisulphite, $\text{ZnSO}_3 \cdot \text{H}_2\text{SO}_3$, then passes into solution. If a solution of this salt be evaporated, and the residue ignited, zinc oxide, free from many of its impurities, will remain. Zinc oxide is a light white powder, used as a paint instead of **white lead**; the basic salt, corresponding with magnesia alba, is used for the same purpose, as also is a mixture of ZnS and BaSO_4 , called lithophone. V. Kouriloff (1890), by boiling the hydrate of the oxide with a 3 per cent. solution of peroxide of hydrogen, obtained $\text{Zn}_2\text{H}_2\text{O}_4$ or the hydrate of the peroxide ($= \text{ZnO}_2 \cdot \text{ZnH}_2\text{O}_2$ or a compound of 2ZnO with H_2O_2), which did not part with its oxygen at 100° , but only above 120° . Cadmium gives a similar compound of a yellow colour. Magnesium, although it forms such a compound, only does so with great difficulty.

³ For the solution of one part of the oxide 55,400 parts of water are required. Nevertheless, even in such a weak solution, zinc oxide (hydroxide, ZnH_2O_2) changes the colour of red litmus paper like a base. Zinc oxide is obtained in the wet way by adding an alkali hydroxide to a solution of a zinc salt; for instance: $\text{ZnSO}_4 + 2\text{KHO} = \text{K}_2\text{SO}_4 + \text{ZnH}_2\text{O}_2$. The gelatinous precipitate of zinc hydroxide is **soluble** in an excess of **alkali** which clearly distinguishes it from magnesia. This solubility of zinc hydroxide in alkalies is due to the power of zinc oxide to form a compound, although an unstable one, with alkalies—that is to say, it points to the fact that zinc oxide already belongs partly to the intermediate oxides. The oxides of the metals above mentioned (except BeO) do not show this property. The property which metallic zinc itself has of dissolving in caustic alkali with the disengagement of hydrogen (the solution is facilitated by contact with platinum or iron) depends on the formation of such a compound of the oxides of zinc and the alkali metals. The solution of zinc hydroxide, ZnH_2O_2 , in potash (in a strong solution), proceeds when these hydrates are taken in the proportion, $\text{ZnH}_2\text{O}_2 + \text{KHO}$. If such a solution is evaporated to dryness, water extracts only caustic potash from the fused residue. When a solution of zinc hydroxide in strong alkali is mixed with a large mass of water, nearly all the oxide of zinc is precipitated; and, therefore, in weak solutions, a large quantity of the alkali is required to effect solution, which points to the decomposition of the zinc-alkali compounds by water (Kouriloff, Rubenbauer, and others). If strong alcohol is added to a solution of zinc oxide in sodium hydroxide, the crystallhydrate, $2\text{Zn(OH)ONa} \cdot 7\text{H}_2\text{O}$, separates. Strong solutions of caustic soda dissolve zinc hydroxide when the two are in the proportion, $\text{Zn(OH)}_2 : 2\text{NaOH}$, that is, when ZnNa_2O_2 is formed; but the solution decomposes spontaneously with the formation of a precipitate, and leaves a solution in which the amount of zinc varies with the concentration, the greatest amount being left when about 3NaHO are taken to Zn(OH)_2 and when there is about half a litre of water to a gram-molecular weight of NaHO . Here, as in other similar instances, the hydroxide undergoes a colloidal transformation.

⁴ **Zinc chloride**, ZnCl_2 , is generally employed in the arts in the form of a solution obtained by dissolving zinc in hydrochloric acid. This solution is used for soldering metals, impregnating railway sleepers, &c. The reason why it is thus employed may be understood from its properties. When evaporated it first parts with its water of crystallisation; on being further heated, however, it loses all traces of water, and forms an oily mass of anhydrous salt which solidifies on cooling. This substance melts at 250° , commences to volatilise at about 400° , and boils at 730° . The soldering of metals—that is, the introduction of an easily fusible metal between two contiguous metallic objects—is hindered by any film of oxide upon them; and, as heated metals easily oxidise, they are naturally difficult to solder. Zinc chloride is used to prevent the oxidation. It fuses on being heated, and, covering the metal with an oily coating, prevents contact with the air; but even if any oxide has formed, the free hydrochloric acid generally existing in the zinc chloride solution dissolves it, and in this way the metallic surface of the metals

combines with ammonium chloride, potassium chloride, &c., just like magnesium chloride, forms an oxychloride, and also combines with zinc oxide.^{4a}

to be soldered is preserved fit for the adhesion of the liquid solder, which on cooling binds the objects together. Much zinc chloride is used also for steeping wood (telegraph posts and railway sleepers) in order to preserve it from decaying quickly. This preservative action is in all probability mainly due to the poisonous character of zinc salts (corrosive sublimate is even more poisonous, and a still better agent to preserve wood from decay), since decay is due to the action of lower organisms. The same object is attained by creosote, phenol, and other substances which hinder the growth of the lower organisms.

The specific gravities of solutions containing p per cent. of zinc chloride, ZnCl_2 , are as follows:—

$p = 10$	20	30	40	50
$15^\circ/4^\circ = 1.093$	1.184	1.293	1.411	1.554
$ds/dt = -3$	-5	-7	-8	-9

The last line shows the change of specific gravity for 1° in ten-thousandth parts for temperatures near 15° . More accurate determinations of Cheltzoff, personally communicated by him, led him to conclude that solutions of zinc chloride follow the same laws as solutions of sulphuric acid, which will be considered in Chap. XX.: (1) from H_2O to $\text{ZnCl}_2, 120\text{H}_2\text{O}$, $s = S_0 + 92.85p + 0.1748p^2$ (2) thence to $\text{ZnCl}_2, 40\text{H}_2\text{O}$, $s = S_0 + 93.96p - 0.0126p^2$; (3) thence to $\text{ZnCl}_2, 25\text{H}_2\text{O}$, $s = 11481.5 + 96.45(p - 15.89) + 0.4567(p - 15.89)^2$; (4) thence to $\text{ZnCl}_2, 10\text{H}_2\text{O}$, $s = 12212.1 + 104.82(p - 23.21) + 0.7992(p - 23.21)^2$; (5) thence to $p = 65$ per cent., $s = 14606.3 + 140.96(p - 43.05) + 1.4905(p - 43.05)^2$, where s is the specific gravity of the solution at 15° , containing p per cent. of ZnCl_2 by weight, taking water at $4^\circ = 10000$, and where $S_0 = 9991.6$ (specific gravity of water at 15°).

Zinc chloride has a great affinity for water; it is not only soluble in it, but also in alcohol, and on being dissolved in water becomes considerably heated, like magnesium and calcium chlorides. Zinc chloride is capable of taking up water, not only in a free state, but also in chemical combination with many substances, and therefore it is used in organic researches for removing the elements of water from many of the organic compounds.

^{4a} When mixed with zinc oxide it forms, with remarkable ease, a very hard mass of **zinc oxychloride**, which is applied in the arts—for instance, in painting—to resist the action of water or for cementing such objects as are destined to remain in water. Zinc oxychloride, $\text{ZnCl}_2, 3\text{ZnO}, 2\text{H}_2\text{O}$ ($= \text{Zn}_2\text{OCl}_2, 2\text{ZnH}_2\text{O}_2$), is also formed from a solution of zinc chloride by the action of a small quantity of ammonia on it after heating the precipitate obtained for a considerable time with the liquid; the admixture of ammonium salts with a mixture of a strong solution of zinc chloride with its oxide makes a similar mass, which does not solidify so rapidly, and is therefore more useful in some cases. Moisture and cold do not change the hardened mass of oxychloride, which also resists the action of many acids and a temperature of 300° , and is hence a useful cement for many purposes. (A solution of magnesium chloride with magnesium oxide forms a similar oxychloride.) The mass solidifies best when there are equal quantities by weight of zinc in the chloride and oxide, and therefore when it has the composition Zn_2OCl_2 . In preparing such a cement, naturally zinc oxide alone may be taken, and the requisite quantity of hydrochloric acid added to it.

The capacity of ZnCl_2 to combine with water, ZnO , and HCl (and also with other metallic chlorides) indicates its property to combine with molecules of other substances, and therefore its compounds with NH_3 , and especially a compound, $\text{ZnCl}_2, 2\text{NH}_3$, similar to sal-ammoniac, might be expected (i.e., $2\text{NH}_4\text{Cl}$, in which H_2 is replaced by Zn). And indeed it has long been known that ZnCl_2 absorbs ammonia and gives solid substances capable of dissociating with the disengagement of NH_3 . Among these compounds

Zinc, like many heavy metals, is often found in nature in combination with sulphur, forming the so-called zinc blende,⁵ ZnS . This sometimes occurs in large masses, often crystallised in cubes; it is frequently translucent, and has a metallic lustre, although this is not so clearly developed as in many other metallic sulphides with which we shall hereafter become acquainted. The ores of zinc also comprise the carbonate and silicate, a mixture of which is known as **calamine**.

Metallic zinc (spelter) is most frequently obtained from the ores containing the carbonate⁶—that is, from calamine, which is sometimes found in thick veins, for instance, in Poland, in Galicia, on the banks of the Rhine, and in considerable masses in Belgium and England. In Russia beds of zinc ore are met with in Poland and the Caucasus, but the output is small. In Sweden, as early as the fifteenth century, calamine was worked up into an alloy of zinc and copper (brass), and Paracelsus produced zinc from calamine; but the technical production of the metal itself, long ago practised in China, only commenced in Europe in 1807—in Belgium, when the Abbé Donnet discovered that zinc was volatile. From that time the production has increased to about 400,000 tons annually.

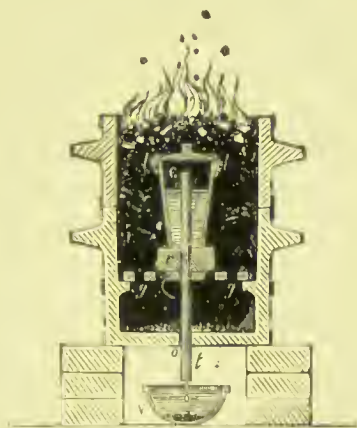


FIG. 90.—Distillation of zinc in a crucible placed in a furnace. *o c*, tube along which the vapour passes and condenses.

The reduction of metallic zinc from its ores is based on the fact Isambert and V. Kouriloff (1894) obtained $\text{ZnCl}_2 \cdot 6\text{NH}_3$, $\text{ZnCl}_2 \cdot 4\text{NH}_3$, $\text{ZnCl}_2 \cdot 2\text{NH}_3$, and $\text{ZnCl}_2 \cdot \text{NH}_3$. The dissociation pressures of the two last-mentioned compounds at 218° are equal to 43.6 mm. and 6.7 mm. respectively. CdCl_2 also forms similar compounds with NH_3 (Kouriloff, 1894).

⁵ This mineral has been given the name of 'mock-ore,' on account of its having the appearance (considerable density, 4.06, &c.) of ordinary metallic ores; it deceived the first miners, because it did not, like other ores, give metal when simply roasted in air and fused with charcoal. The white zinc oxide, formed by burning the vapours of zinc, was also called 'nihil album,' or 'white nothing,' on account of its lightness.

⁶ It may here be mentioned that by the word **ore** is meant a hard, heavy substance, which is dug out of the earth and used in metallurgical works for obtaining the ordinary heavy metals long known and used. The natural compounds of sodium or magnesium are not called ores, because magnesium and sodium have not been long obtainable in quantity. The heavy metals, which are easily reduced and do not easily oxidise, are those which are exclusively directly applied in manufactures. Ores either contain the metals themselves (for instance, ores of silver or bismuth), and the metals are then said to be in a native state, or else their sulphur compounds (blende, mock-ore, pyrites—as, for example, galena, PbS ; zinc blende, ZnS ; copper pyrites, CuFeS) or oxides (as the ores of iron), or salts (calamine, for instance). Zinc is incomparably rarer than magnesium, and is only well known because it is transformed from its ores into a metal which finds direct use in many branches of industry.

that zinc oxide⁷ is easily reduced by charcoal at a red heat: $\text{ZnO} + \text{C} = \text{Zn} + \text{CO}$. The zinc thus obtained is in a finely divided state and impure, being mixed with other metals reduced with it, but the greater portion is **converted into vapour**, from which it easily passes into a liquid or solid state. The reduction and distillation are carried on in earthenware retorts, filled with a mixture of the divided ore and charcoal. The vapours of zinc and gases formed during the reaction escape by means of a pipe leading downwards, and are led to a chamber where the vapours are cooled. By this means they do not come into contact with the air, because the neck of the retort is filled with gaseous carbonic oxide, and therefore the zinc does not oxidise; otherwise its vapour would burn in the air.^{7a} The vapours of zinc, entering the cooling chamber, condense into white zinc powder or zinc dust. When the neck of the retort is heated the zinc is obtained in a liquid state, and is cast into plates, in which form it is generally sold.

Commercial zinc is generally impure, containing lead, arsenic, particles of carbon, iron, and other metals carried over with the vapours, although they are not volatile at a temperature approaching 1000° , at which zinc is volatilised. If it be required to obtain pure zinc from the commercial article, the latter is subjected to a further slow distillation in a crucible with a pipe passing through the bottom, the vapours formed by the heated zinc only having exit through the pipe cemented into the bottom of the crucible, if the covers are properly luted on. Passing through this pipe, the vapours condense to a liquid, which is collected in a receiver. Zinc thus purified is generally re-melted and cast into rods, and in this form is often used for physical and chemical researches where a pure article is required.⁸

⁷ After being extracted from the earth by the miners, ores are often enriched by sorting, washing, and other mechanical operations. The sulphurous ores (and likewise others) are then generally roasted. Roasting an ore means heating it to redness in air. The sulphur then burns, and passes off in the form of sulphurous anhydride, SO_2 , and the metal oxidises. The roasting is carried on in order to obtain an oxide instead of a sulphur compound, the oxide being reducible by charcoal. These methods, introduced ages ago, are met with in nearly all metallurgical works for practically all ores. For this reason the preparatory treatment of zinc blende furnishes zinc oxide: this is already contained in calamine.

^{7a} With very impure ores, especially such as contain lead (PbS often accompanies zinc), the vapour of the reduced zinc is allowed to pass directly into the air. It burns and gives ZnO , which is used as a pigment. A considerable amount of zinc is now obtained by electrolysis, by the action of an electric current on solutions of chloride of zinc, which is obtained as a by-product from the ores of other metals in separating the zinc they contain by hydrochloric acid. The zinc obtained by electrolysis is generally purer than that prepared by volatilisation. Further details will be found in works on electro-metallurgy.

⁸ This zinc, although homogeneous, still contains certain impurities, to remove which

Metallic zinc has a bluish-white colour ; its lustre, compared with that of many other metals, is insignificant. When cast it exhibits a crystalline structure. Its specific gravity is about 7, varying from 6·8 to 7·2, according to the degree of compression (by forging, rolling, &c.) to which it has been subjected. It is very ductile, considering its hardness. For this reason it chokes up files when being worked. Its malleability is considerable when pure, but in the ordinary impure condition in which it is sold, it is impossible to roll it at the ordinary temperature, as it easily breaks. At a temperature of 100° , however, it easily undergoes such operations, and can then be drawn into wire or rolled into sheets. If heated further it again becomes brittle, and at 200° may be even crushed into powder, so completely does it lose its molecular cohesion. It melts at 418° , and distils at 930° .

Zinc does not undergo any change in the atmosphere. Even in very damp air it only becomes coated with a thin white coating of oxide. For this reason it is available for all objects which are only in contact with air. Sheet zinc may therefore be used for roofing and many other purposes.⁹ This great stability of zinc in air shows its slight energy with regard to oxygen as compared with the metals already mentioned, which are capable of reducing zinc from solutions. But zinc plays this part with regard to the remaining metals ; for example, it reduces salts of lead, copper, mercury, &c. Although zinc is an almost unoxidisable metal at the ordinary temperature, it burns in the air on being heated, particularly when in the form of shavings or in the condition of vapour. At the ordinary temperature zinc does not decompose water—at any rate, if the metal is in a dense mass. But even at a temperature of 100° zinc begins little by little to decompose water ; it easily displaces the hydrogen of acids at the ordinary temperature, and that of alkalis on being heated.

In this respect the action of zinc varies a great deal with the degree of its purity. Weak sulphuric acid (corresponding with the

it is necessary to prepare some salt of zinc in a pure state and transform it into carbonate, which latter is then distilled with charcoal ; and, as thin sheets of zinc can only be obtained from very pure metal, they are frequently made use of in cases where pure zinc is required. In order to remove the arsenic from zinc, it was proposed to melt it and mix it with anhydrous magnesium chloride, by which means vapours of zinc chloride and arsenic chloride are formed. Perfectly pure zinc is made (V. Meyer and others) by decomposing, by means of the galvanic current, a solution of zinc sulphate to which an excess of ammonia has been added. The zinc used for Marsh's arsenic test (Chap. XIX.) is purified from As by fusing it with KNO_3 and then with ZnCl_2 .

⁹ Cornices and other architectural ornaments, remarkable for their lightness and beauty, are stamped out of sheet zinc. Zinc-roofing does not require painting, but it melts during a conflagration, and even burns at a strong heat. Many iron vessels, &c., are covered with zinc ('galvanised') in order to prevent them from rusting.

composition $\text{H}_2\text{SO}_4, 8\text{H}_2\text{O}$) at the ordinary temperature does not act at all on chemically pure zinc, and even a stronger solution acts very slowly. If the temperature be raised, and particularly if the zinc be previously slightly heated, so as to cover the surface with a film of oxide, chemically pure zinc acts on sulphuric acid. Thus, for example, one cubic centimetre of zinc in sulphuric acid having a composition $\text{H}_2\text{SO}_4, 6\text{H}_2\text{O}$ at the ordinary temperature in two hours only dissolves to the extent of 0.018 gram, and at a temperature of 100° , of about 3.5 grams. If we compare this slow action with that rapid evolution of hydrogen which occurs in the case of commercial zinc, we see that the influence of the impurities in the zinc is very great. Every particle of charcoal or iron introduced into the mass of the zinc, and likewise the connection of the zinc with a piece of another electro-negative metal, assist such a dissolution. The slowness of the action of sulphuric acid on pure zinc (and likewise on amalgamated zinc) may also be explained by the fact that a layer of hydrogen¹⁰ collects on the surface of the metal, preventing contact between the acid and the metal.^{10a}

¹⁰ Veeren (1891) proved this by simple experiments, finding that *in vacuo* the solution proceeds far more rapidly for both pure and commercial zinc, and still more rapidly in the presence of oxidising agents (which absorb the hydrogen) like CrO_3 and H_2O_2 .

^{10a} The addition of cupric sulphate, or, better still, a few drops of platinic chloride (the metals become reduced), to the sulphuric acid greatly accelerates the evolution of the hydrogen, because in this case, as with commercial zinc, galvanic couples are formed locally by the copper or platinum and the zinc, under the influence of which the zinc rapidly dissolves. The action of acids on metallic zinc of various degrees of purity has been the subject of many investigations, particularly important with reference to the application of zinc in galvanic batteries, whilst some investigations have direct significance for chemical mechanics, although from many points of view the matter is not clear. I consider it useful to mention certain of these investigations.

Calvert and Johnson made the following series of observations on the action of sulphuric acid of various degrees of concentration on 2 grams of pure zinc during two hours. In the cold the concentrated acid, H_2SO_4 , does not act, $\text{H}_2\text{SO}_4, 2\text{H}_2\text{O}$ dissolves about 0.002 gram, but forms principally hydrogen sulphide, which is obtained also when the dilution reaches $\text{H}_2\text{SO}_4, 7\text{H}_2\text{O}$, at which 0.035 gram of zinc is dissolved. When the acid is largely diluted with water, pure hydrogen begins to be disengaged. $\text{H}_2\text{SO}_4, 2\text{H}_2\text{O}$ at 130° gives a mixture of hydrogen sulphide and sulphurous anhydride and dissolves 0.156 gram of zinc.

Bouchardat showed that if, in a vessel made of glass or sulphur, dilute sulphuric acid acting on a piece of zinc liberate one part of hydrogen, the same acid with the same piece of zinc in the same time will liberate 4 parts of hydrogen if the vessel be made of tin, with which the zinc forms a galvanic couple; in a leaden vessel 9 parts of hydrogen are set free, with one of antimony or bismuth 13 parts, with silver or platinum 38 parts, with copper 50 parts, and with iron 43 parts. Millon determined that if a salt of platinum is added to the dilute sulphuric acid (1 part of acid and 12 parts of water), the rapidity of the action on the zinc is increased 149 times, and by the addition of copper sulphate the action is rendered 45 times greater than that of pure sulphuric acid. The salts which are added are reduced to metals by the zinc, their contact serving to promote the reaction owing to the formation of local galvanic currents.

The action of zinc on acids, and the consequent formation of zinc salts, interfere with its application in many cases, particularly for the

According to the observations of Cailletet, if, at the ordinary pressure, sulphuric acid with zinc liberates 100 parts of hydrogen, then with a pressure of 60 atmospheres 47 parts will be liberated, and at a pressure of 120 atmospheres 1 part. With a reduced pressure under the receiver of an air-pump 168 parts are liberated. Helmholtz showed that a reduced pressure also exercises an influence on galvanic elements.

Debray, Löwel, and others showed that zinc liberates hydrogen and forms basic salts and zinc oxide with solutions of many salts; for instance, MCl_n , aluminium sulphate, and alum. Sodium and potassium carbonates scarcely act at all, because they form carbonates. The salts of ammonia act more strongly than those of potassium and sodium; the zinc remains bright. It is evident that this action is founded on the formation of double and basic salts.

The variation with concentration in the rate of the action of sulphuric acid on zinc (containing impurities) under otherwise uniform conditions is in evident connection with the electrical conductivity of the solution and its viscosity, although, when largely diluted, the action is almost proportional to the amount of acid in a known volume of the solution. Forging, casting the molten metal, and similar mechanical influences change the density and hardness of zinc, and also strongly influence its power of liberating hydrogen from acids. Kayander showed (1881) that when magnesium is submitted to the action of acids: (a) the action depends, not on the nature of the acid, but on its basicity; (b) the increase of the action is more rapid than the growth of the concentration; and (c) there is a decrease of action with an increase of the coefficient of internal friction and electrical conductivity.

Spring and Aubel (1887) measured the volume of hydrogen disengaged by an alloy of zinc and a small quantity of lead (0.6 per cent.), because the action of acids is then uniform. In order to deal with a known surface, spheres were taken (9.5 millimetres diameter) and cylinders (17 mm. diam.), the sides of which were covered with wax in order to limit the action to the end surfaces. During the commencement of the action of a definite quantity of acid the rapidity increases, attains a maximum, and then declines as the acid becomes exhausted. The results for 5, 10, and 15 per cent. of hydrochloric acid are given below. H denotes the number of cubic centimetres of hydrogen, D the time in seconds elapsing after the zinc spheres have been plunged into the acid.

At 15° were obtained:

H = 50	100	200	400	600	800	1000
5 per cent. D = 714	1152	1755	2731	3908	6234	15462
10 per cent. D = 301	455	649	995	1573	2746	6748
15 per cent. D = 106	151	233	440	826	1604	4289

At 35°:

5 per cent. D = 462	705	1058	1700	2525	4182	8499
10 per cent. D = 96	148	239	460	835	1594	3735
15 per cent. D = 44	64	112	255	505	1011	2457

At 55°:

5 per cent. D = 178	276	408	699	1164	2105	5093
10 per cent. D = 34	60	113	258	491	970	2457
15 per cent. D = 24	35	58	136	239	610	1593

In consequence of the complex character of the phenomenon, the authors themselves do not consider their determinations as being conclusive, and only give them a relative significance; and in this connection it is remarkable that hydrobromic acid under similar conditions (with an equivalent strength) gives a greater (from 2 to 5 times) rapidity of action than hydrochloric acid, but sulphuric acid a far smaller velocity (nearly 25 times smaller). It is also remarkable that during the reaction the metal becomes much more heated than the acid.

preservation of liquids either containing or capable of developing acid. For this reason zinc vessels ought not to be used for the preparation or preservation of food substances, as these often contain or yield acids which form poisonous salts with the zinc. Even ordinary water, containing carbonic acid, slowly attacks and corrodes zinc.

Finally divided zinc, or **zinc dust**, obtained in the distillation of the metal when the receiver is not heated up to the melting-point, on account of its presenting a large surface of contact and containing foreign matter (particularly zinc oxide), has in the highest degree the property of acting on acids, and even water, which it easily decomposes, particularly if slightly heated. On this account zinc dust is often used in laboratories and factories as a reducing agent. A similar influence of the finely divided state is also noticed in other metals—for instance, copper and silver—which again shows the close connection between chemical and physico-mechanical phenomena. We must first of all turn to this close connection for an explanation of the widespread application of zinc in galvanic batteries, where the chemical (latent, potential) energy of the acting substances is transformed into (evident, kinetic) galvanic energy, and through this latter into heat, light, or mechanical work.

Hermann and Stromeyer, in 1819, showed that **cadmium** is almost always found with zinc, and in many respects resembles it. When distilled the cadmium volatilises sooner, because it has a lower boiling-point. Sometimes the zinc dust obtained by the first distillation of zinc contains as much as 5 per cent. of cadmium. When zinc blende, containing cadmium, is roasted, the zinc passes into the state of oxide, and the cadmium sulphide in the ore oxidises to cadmium sulphate, CdSO_4 , which resists tolerably well the action of heat; therefore if roasted zinc blende be washed with water, a solution of cadmium sulphate will be obtained, from which it is very easy to prepare metallic cadmium. Hydrogen sulphide may be used for separating cadmium from its solutions; it gives a **yellow precipitate of cadmium sulphide**, CdS (according to the equation $\text{CdSO}_4 + \text{H}_2\text{S} = \text{H}_2\text{SO}_4 + \text{CdS}$),¹¹ which, on account of its characteristic colour, is used as a pigment.^{11a}

It may be mentioned that zinc dust or zinc itself, when heated with hydrated lime and similar hydrates, disengages hydrogen: this method has even been proposed for obtaining hydrogen for filling war balloons.

¹¹ It may be here remarked that sulphate of zinc (especially in the presence of mineral acids, which decompose ZnS) does not give a precipitate of sulphide of zinc, or is only slightly precipitated by sulphuretted hydrogen.

^{11a} Sulphide of cadmium appears in two varieties of a similar chemical but different physical character: one is of a lemon colour, and the other red. Kloboukoff (1890) studied the physical properties of these varieties more closely. The sp. gr. of the former

Cadmium sulphide, when strongly heated in air, leaves cadmium oxide, from which the metal may be obtained in precisely the same way as in the case of zinc.

Cadmium is a white metal, and when freshly cut is almost as white and lustrous as tin. It is so soft that it may be easily cut with a knife, and so malleable that it can be easily drawn into wire, rolled into sheets, &c. Its specific gravity is 8.67, melting-point 320° , boiling point 770° ; its vapours burn, forming a brown powder of the oxide.¹² Next to mercury it is the most volatile metal; hence Deville determined the density of its vapours compared with hydrogen, and found it to be equal to 57.1; therefore the molecule contains **one atom** whose weight is 112. V. Meyer found the like for zinc; the molecule of mercury also contains one atom.

Mercury resembles zinc and cadmium in many respects, but presents that distinction from them which is always noticed in all the heaviest metals (with regard to atomic weight and density) compared with the lighter ones—namely, that it oxidises with more difficulty, and its compounds are more easily decomposed.^{12a} Besides compounds of the

is 3.906, and that of the latter 4.513. They belong to different crystallographic systems. The first variety may be converted into the second by friction or pressure, but the second cannot be converted into the first variety by these means.

¹² Of the compounds of cadmium very closely allied to the compounds of zinc, we must mention **cadmium iodide**, CdI_2 , which is used in medicine and photography. This salt crystallises very well; it is prepared by the direct action of iodine, mixed with water, on metallic cadmium. One part of cadmium iodide at 20° requires for its solution 1.08 part of water. Cadmium chloride at the same temperature requires 0.71 part of water to dissolve it, so that the iodine compound of this metal is less soluble than the chloride, whilst the reverse relation holds in the case of the corresponding compounds of the alkali or alkaline earth metals. *Cadmium sulphate* crystallises well, and has the composition $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$, thus differing from zinc sulphate.

Cadmium oxide is soluble, although sparingly, in alkalis, but in the presence of tartaric and certain other acids the alkaline solution of cadmium oxide does not change when boiled, whilst a *diluted* solution in that case deposits cadmium oxide: this may also serve for separating zinc from cadmium. The latter is precipitated from its salts by zinc, so that from an alloy of zinc and cadmium, acids first of all extract the zinc. Cadmium is in all respects less energetic than zinc. Thus, for instance, it decomposes water with difficulty, and only when strongly heated. It even acts but slowly on acids, but then displaces hydrogen from them. It is necessary here to call attention to the fact that for alkali and alkaline earth metals (of the even series) the highest atomic weight determines the greatest energy; but cadmium (of the uneven series), whilst having a larger atomic weight than zinc, is less energetic. The salts of cadmium are colourless, like those of zinc. De Schulten obtained a crystalline oxychloride, $\text{Cd}(\text{OH})\text{Cl}$, by heating marble with a solution of cadmium chloride in a sealed tube at 200° . It is notable that even very dilute solutions (0.2 per cent.) of CdCl_2 (and also of CdBr_2 , CuCl_2 , HgCl_2 , &c.), are precipitated by an excess of strong sulphuric acid, so that a reagent for detecting traces of any chloride may be prepared by mixing 1 vol. of a 10 per cent. solution of CdSO_4 with 10 vols. of H_2SO_4 .

^{12a} According to its atomic weight, mercury follows gold in the periodic system, just as cadmium follows silver and zinc follows copper:—

usual type RX_2 , it also gives those of the lower type, RX , which are unknown for zinc.¹³ Mercury therefore gives salts of the composition HgX (mercurous salts) and HgX_2 (mercuric salts), the oxides having the formulæ Hg_2O and HgO respectively.

Mercury is found in nature almost exclusively in combination with sulphur (like zinc and cadmium, but is still rarer than them) in the form known as cinnabar, HgS (Chap. XX., note 29). It is far more rarely met with in the native or metallic condition, and this in all probability has been derived from cinnabar. Mercury ore is found only in a few places—namely, in Spain (in Almaden), in Illyria, Japan, Peru, and California. About the year 1880 Minenkoff discovered a rich bed of cinnabar in the Bahmout district (near the station of Nikitovka), in the government of Ekaterinoslav, so that now Russia even exports mercury to other countries. Cinnabar is now also being worked in Daghestan in the Caucasus. Mercury ores are easily reduced to metallic mercury, because the combination between the metal and the sulphur is one of but little stability. Oxygen, iron, lime, and many other substances, when heated, easily destroy the combination. If iron is heated with cinnabar, iron sulphide is formed; if cinnabar is heated with lime, mercury and calcium sulphide and sulphate are formed, $4HgS + 4CaO = 4Hg + 3CaS + CaSO_4$. On being heated in the air, or roasted, the sulphur burns, oxidises, forming sulphurous anhydride, and vapours of metallic mercury are formed. Mercury is more easily distilled than all other metals, its boiling-point being about 351° , and its separation from natural admixtures after decomposition by one of the above-mentioned methods is therefore effected at the expense of a comparatively small amount of heat. The mixture of mercury vapour,

Ni = 59	Cu = 63	Zn = 65
Pd = 106	Ag = 108	Cd = 112
Pt = 195	Au = 197	Hg = 200

Eventually we shall see the near relation of platinum, palladium, and nickel, and also of gold, silver, and copper, but we shall now point out the parallelism between these three groups. The relations between the physical and also the chemical properties are here strikingly similar. Nickel, palladium, and platinum are very difficult to fuse (far more so than iron, ruthenium, and osmium, which stand before them). Copper, silver, and gold melt far more easily in a strong heat than the three preceding metals, and zinc, cadmium, and mercury melt still more easily. Nickel, palladium, and platinum are very slightly volatile; copper, silver, and gold are more volatile; and zinc, cadmium, and mercury are among the most volatile metals. Zinc oxidises more easily than copper, and is reduced with more difficulty, and the same is true for mercury as compared with gold. These properties for cadmium and silver are intermediate in the respective groups. Relations of this kind clearly show the reality of the periodic law.

¹³ Thus thallium, lead, and bismuth, following mercury according to their atomic weights, form, besides compounds of the highest types, TlX_3 , PbX_4 , and BiX_5 , also the lower ones TlX , PbX_2 , and BiX_3 . Cadmium, as the nearest analogue of Hg, also gives a lower oxide, formed by calcining the oxalate.

air, and products of combustion obtained is cooled in tubes (by water or air), in which the mercury condenses as liquid metal.¹⁴ About 4,000 tons of mercury are produced yearly by the mines of the world.

Mercury, as everybody knows, is a liquid metal at the ordinary temperature. In its lustre and whiteness it resembles silver.¹⁵ It boils at $+357^{\circ}$. At -39° mercury is transformed into a malleable crystalline metal; at 0° its specific gravity is 13.596, and in the solid state at -40° it is 14.39.¹⁶ Mercury does not change in the air—that is to say, it does not oxidise at the ordinary temperature—but at a temperature approaching the boiling-point, as was stated in the Introduction, it oxidises, forming mercuric oxide. Both metallic mercury and its compounds in general produce salivation, trembling of the hands, and other unhealthy symptoms which are found in the workmen exposed to the influence of mercurial vapours¹⁷ or the dust of its compounds.

As many of the compounds of mercury decompose on being heated

¹⁴ During the condensation of the vapours of mercury in works, a part forms a black mass of finely divided particles, which gives metallic mercury when worked up in centrifugal machines, or when compressed or re-distilled. In mercury we observe a tendency to split up easily into the finest drops, which are difficult to unite into a dense mass. It is sufficient to shake up mercury with nitric and sulphuric acids in order to produce such a mercury *powder*. The mercury separated (for instance, reduced by substances like sulphurous anhydride) from solutions forms such a powder. According to the experiments of Nernst, this disintegrated mercury when entering into reactions develops more heat than the dense liquid metal; that is say, the work of disintegration reappears in the form of heat. This example is instructive in considering thermo-chemical deductions.

¹⁵ Mercury may sometimes be obtained in a perfectly pure state from works (in iron bottles holding about 35 kilos), but after being used in laboratories (for baths, calibration, &c.) it contains impurities. It may be purified mechanically in the following way: a paper filter with a fine hole (pricked with a needle) is placed in a glass funnel and into it is poured mercury, which slowly trickles through the hole, leaving the impurities upon the filter. Sometimes it is squeezed through chamois leather or through a block of wood (as in the well-known experiment with the air-pump). It may be purified from many metals by contact with dilute nitric acid, if small drops of mercury are allowed to pass through a long column of it (from the fine end of a funnel); or by shaking it up with sulphuric acid in air. Mercury may be purified by the action of an electric current, if it be covered with a solution of HgNO_3 . But the complete purification of mercury for barometers and thermometers can only be attained by distillation, best in a vacuum (the vapour pressure of mercury is given in Chap. II., note 27). For this purpose Weinhold's apparatus is most often used. The principle of this apparatus is very ingenious, the distillation being effected in a Torricellian vacuum continuously supplied with fresh mercury, while the condensed mercury is continuously removed. This process of distillation requires very little attention, and gives about one kilo of pure mercury per hour.

¹⁶ If the volume of *liquid* mercury at 0° be taken as 1000000, then, according to the determinations of Regnault (re-calculated by me in 1875), at t° it will be $1000000 + 180.1t + 0.02t^2$, or $1000000 + 181.6t + 0.08t^2$ according to Tuson.

¹⁷ The alchemists called mercury '*mercurii*,' and this name has been adopted in science instead of the popular term '*quicksilver*.'

—for instance, the oxide or carbonate¹⁸—and as zinc, cadmium, copper, iron, and other metals separate mercury from its salts,¹⁹ it is evident that mercury has less chemical energy than the metals already described, even than zinc and cadmium. Nitric acid, when acting on an excess of mercury at the ordinary temperature, gives mercurous nitrate, HgNO_3 .²⁰ The same acid, under the influence of heat and when in excess (nitric oxide being liberated), forms mercuric nitrate, $\text{Hg}(\text{NO}_3)_2$. This,²¹ both in its composition and properties, resembles the salts of zinc and cadmium. Dilute sulphuric acid does not act on mercury, but strong sulphuric acid dissolves it, with evolution of sulphurous anhydride (not hydrogen), and on being slightly heated with an excess of mercury it forms the sparingly soluble mercurous sulphate, Hg_2SO_4 ; but if mercury is strongly heated with an excess of the acid, the mercuric salt, HgSO_4 ,²² is formed. Alkalies do not act on mercury, but the non-metals chlorine, bromine, sulphur, and phosphorus easily combine with it. They yield, like the acids, two series of compounds, HgX and HgX_2 . The oxygen compound of the first series is the suboxide of mercury, or mercurous oxide, Hg_2O , and

¹⁸ All salts of mercury, when mixed with sodium carbonate and heated, decompose, forming carbonic anhydride, oxygen, and vapours of mercury.

¹⁹ Spring (1888) showed that solid dry HgCl is gradually decomposed in contact with metallic copper. According to the determinations of Thomsen, the formation of a gram of mercurial compounds from their elements develops the following amounts of heat (in thousands of units): $\text{Hg}_2 + \text{O}$, 42; $\text{Hg} + \text{O}$, 31; $\text{Hg} + \text{S}$, 17; $\text{Hg} + \text{Cl}$, 41; $\text{Hg} + \text{Br}$, 34; $\text{Hg} + \text{I}$, 24; $\text{Hg} + \text{Cl}_2$, 63; $\text{Hg} + \text{Br}_2$, 51; $\text{Hg} + \text{I}_2$, 34; $\text{Hg} + \text{C}_2\text{N}_2$, 19. These numbers are less than the corresponding ones for potassium, sodium, calcium, barium, and for zinc and cadmium—for instance, $\text{Zn} + \text{O}$, 85; $\text{Zn} + \text{Cl}_2$, 97; $\text{Zn} + \text{Br}_2$, 76; $\text{Zn} + \text{I}_2$, 49; $\text{Cd} + \text{Cl}_2$, 93; $\text{Cd} + \text{Br}_2$, 75; $\text{Cd} + \text{I}_2$, 49.

²⁰ This salt easily forms the crystallo-hydrate $\text{HgNO}_3 \cdot \text{H}_2\text{O}$, corresponding with ortho-nitric acid, H_3NO_4 (the terms ortho-, pyro-, and meta-acids are explained in the chapter on Phosphorus), with the substitution of Hg for H. In an aqueous solution this salt can only be preserved in the presence of free mercury, otherwise it forms basic salts of the oxide, which will be mentioned hereafter.

²¹ Mercuric nitrate, $\text{Hg}(\text{NO}_3)_2 \cdot 8\text{H}_2\text{O}$, crystallises from a concentrated solution of mercury in an excess of boiling nitric acid. Water decomposes this salt; at the ordinary temperature crystals of a basic salt of the composition $\text{Hg}(\text{NO}_3)_2 \cdot \text{HgO} \cdot 2\text{H}_2\text{O}$ are formed, and with an excess of water the insoluble yellow basic salt $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O} \cdot 2\text{HgO}$. These three salts correspond with the type of ortho-nitric acid, $(\text{H}_3\text{NO}_4)_2$, in which mercury is substituted for 1, 2, and 3 times H_2 .

²² To obtain the mercuric salt a large excess of strong sulphuric acid must be taken and strongly heated. With a small quantity of water colourless crystals of $\text{HgSO}_4 \cdot \text{H}_2\text{O}$ may be obtained. An excess of water, especially when heated, forms the basic salt (as in note 21), $\text{HgSO}_4 \cdot 2\text{HgO}$, which corresponds with trihydrated sulphuric acid, $\text{SO}_3 + 3\text{H}_2\text{O} = \text{S}(\text{OH})_6$, with the substitution of H_2 by 3Hg , which in mercuric salts are equivalents. Le Chatelier (1888) gives the following ratios between the amounts of equivalents per litre:

HgSO_4	.	.	0.318	0.890	1.80	2.02
SO_3	.	.	0.752	1.42	2.10	2.40

—that is, the relative amount of free acid decreases as the strength of the solution increases.

that of the second order the oxide HgO , mercuric oxide. The chlorine compound corresponding with the suboxide is HgCl (calomel), and with the oxide HgCl_2 (corrosive sublimate or mercuric chloride). In the compounds HgX , mercury is univalent and resembles the metals of the first group, and more especially silver. In the mercuric compounds there is an evident resemblance to those of magnesium, cadmium, &c. Here the atom of mercury is bivalent, as in the type RX_2 .²³ Every

²³ The molecular weight of calomel was a contested point of great interest in chemistry during the eighties and the beginning of the nineties of the last century, because in those days there were many chemists who argued from the fact of C being generally quadrivalent in the carbon compounds (forgetting CO), that the atomicity of the elements (Chap. X., note 1) must be a constant, fundamental, and unchangeable property of the elementary atoms, and that therefore Hg must be exclusively divalent, because it gives mercury ethyl, $\text{Hg}(\text{C}_2\text{H}_5)_2$, and corrosive sublimate, HgCl_2 , about the molecular weight of which there could be no doubt (judging by the reactions and the vapour densities). But as calomel, HgCl , is volatile, and its vapour density (about 118 if $\text{H} = 1$) indicates its molecular composition to be HgCl , it is necessary to regard the mercury in it as univalent. Endeavours were made to explain this by saying that the molecule of calomel contains Hg_2Cl_2 , and that its vapour does not contain true calomel, Hg_2Cl_2 , but only the products of its decomposition, corrosive sublimate and mercury, $\text{Hg}_2\text{Cl}_2 = \text{HgCl}_2 + \text{Hg}$. This would render it possible to consider mercury as divalent in all its compounds, because calomel would then be regarded as a compound of two residues (radicles), HgCl , of corrosive sublimate in which mercury is diatomic (like two residues of CH_4 in C_2H_6 , Chap. VIII.). Moreover, the vapour density of calomel (under its assumed decomposition) should, indeed, be about 118, for that of corrosive sublimate is about 136, and that of mercury 100, so that the value for calomel would be half their sum. Efforts were made, and with some success, to confirm this hypothesis (and similar ones were often adopted for other elements in those days) by experiment in order to corroborate a false theory, namely, the constancy of the atomicity of the elements. The researches of V. Meyer and Harris (1894) were particularly convincing in this respect. They showed (1) that more mercury vapour than chlorine is diffused through the pores of an earthenware vessel in which calomel is volatilised at 465° , so that some corrosive sublimate must have remained in the vessel; and (2) that a hot piece of KHO introduced into the vapour of calomel gives yellow oxide of mercury, and not the black suboxide, whence they concluded that the vapour contains no calomel, but only a mixture of the vapours of corrosive sublimate and mercury. The evidence given by these experiments is doubtful, first, because the difference between the rates of diffusion of the vapours of Hg and HgCl is infinitesimal (for the vapour densities are very much alike, and their square roots still more so); and, secondly, the suboxide of mercury (see text) and the compounds corresponding to it are unstable and easily pass into (even under the action of light) the oxide and metallic mercury. So that there is every reason for supposing that a portion of the calomel HgCl exists in the vapour and a portion decomposes (a state of equilibrium sets in); but there is no cause for assuming entire decomposition, for there can be no doubt that there are vapours and gases whose molecules prove the possibility of elements having more than one form of atomicity, for instance, CO and CO_2 ; N_2O , NO, and NH_3 ; PCl_3 and PCl_5 or PF_3 , &c. So that, speaking in general terms, a constant atomicity in the elements is not in the nature of things, and this apparent constancy can only be looked upon as a method of former days, having its historical interest as a means of incentive to research. Concerning the molecular weight of calomel in particular, there is no foundation for assuming this to be other than HgCl , according to the results of direct experiment; and if it is found that its vapour contains Hg and HgCl_2 (*in toto* or *in part*), this does not interfere with the modern chemical notions of the variability of atomicity.

soluble mercurous compound (corresponding with the type of the sub-oxide of mercury), HgX , forms a white precipitate of calomel, HgCl , with hydrochloric acid or a metallic chloride, because HgCl is very slightly soluble in water, $\text{HgX} + \text{MCl} = \text{HgCl} + \text{MX}$. With soluble mercuric compounds, HgX_2 , hydrochloric acid and metallic chlorides do not form a precipitate, because corrosive sublimate, HgCl_2 , is soluble in water. Alkali hydroxides precipitate the yellow mercuric oxide from a solution of HgX_2 , and the black mercurous oxide from one of HgX . Potassium iodide forms a dirty greenish precipitate, HgI , with mercurous salts, HgX , and a red precipitate, HgI_2 , with the mercuric salts, HgX_2 . These reactions distinguish the mercuric from the mercurous salts, which latter represent the transition from the mercuric salts to mercury itself, $2\text{HgX} = \text{Hg} + \text{HgX}_2$. The salts, HgX , as well as HgX_2 , are reduced by nascent hydrogen (e.g., from $\text{Zn} + \text{H}_2\text{SO}_4$), by such metals as zinc and copper, and also by many other reducing agents—for example, hypophosphorous acid, the lowest grade of oxidation of phosphorus, by sulphurous anhydride, stannous chloride, &c. Under the action of these reagents the mercuric salts are generally first transformed into the mercurous salts, and the latter then reduced to metallic mercury. This reaction is so delicate that it serves to detect the smallest quantity of mercury; for instance, in cases of poisoning, the mercury is detected by immersing a copper plate in the solution to be tested, the mercury being then deposited upon it (more readily on passing a galvanic current). The copper plate, on being rubbed, shows a silvery white colour; on being heated, it yields vapours of mercury, and then again assumes its original red colour (if it does not oxidise). The mercurous compounds, HgX , under the action of oxidising agents, even air, pass into mercuric compounds, especially in the presence of acids (otherwise a basic salt is produced), $2\text{HgX} + 2\text{HX} + \text{O} = 2\text{HgX}_2 + \text{H}_2\text{O}$; but the mercuric compounds, when in contact with mercury, undergo change more or less readily, and turn into mercurous compounds, $\text{HgX}_2 + \text{Hg} = 2\text{HgX}$. For this reason, in order to preserve solutions of mercurous salts, a little mercury is generally added to them.

The lowest oxygen compound of mercury—that is, **mercurous oxide**, Hg_2O —apparently only exists in a transient form, for the substance precipitated in the form of a black mass by the action of alkalis on a solution of mercurous salts decomposes on keeping (especially in sunlight) into the yellow mercuric oxide and metallic mercury, and then acts as a simple mechanical mixture of oxide, HgO , with mercury (Guibourt, and others). The other compound of mercury with oxygen

is already known to us as **mercuric oxide**, HgO , obtained in the form of a red crystalline substance by the oxidation of mercury in the air, and precipitated as a yellow powder by the action of sodium hydroxide on solutions of salts of the type HgX_2 . In this case it is amorphous and more amenable to the action of various reagents (Chap. XI, note 32) than when it is in the crystalline state. Indeed, on trituration, the red oxide is changed into a powder of a yellow colour. It is very sparingly soluble in water, and forms an alkaline solution which precipitates magnesia from the solution of its salts.

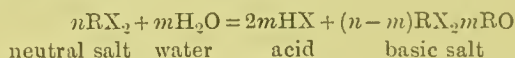
Mercury combines directly with chlorine, and the first product of combination is **calomel** or mercurous chloride, HgCl . This is obtained, as above stated, in the form of a white precipitate by mixing solutions of mercurous salts with hydrochloric acid or with metallic chlorides. A precipitate of calomel is also obtained by reducing a boiling aqueous solution of corrosive sublimate, HgCl_2 , with sulphurous anhydride. It is likewise produced by heating corrosive sublimate with mercury.^{23a} Calomel may be distilled. In the solid state its specific gravity is 7.0; it crystallises in rhombic prisms, is colourless, but has a yellowish reflection, turns brown from the action of light, and when boiled with hydrochloric acid decomposes into mercury and corrosive sublimate. It is used as a strong purgative. **Corrosive sublimate** or mercuric chloride, HgCl_2 , can be obtained from or converted into calomel by many methods.²⁴ An excess of chlorine (for instance, *aqua regia*) converts calomel and also mercury into corrosive sublimate. It owes its name corrosive sublimate to its volatility, and, in medicine up to the present day, it is termed *Mercurius sublimatus seu corrosivus*. The vapour density, compared with that of hydrogen, is 135, so that its molecule is HgCl_2 . It forms colourless prismatic crystals of the rhombic system, boils at 307° , and is soluble in alcohol. It is usually prepared by subliming a mixture of mercuric sulphate with common salt, $\text{HgSO}_4 + 2\text{NaCl} = \text{Na}_2\text{SO}_4 + \text{HgCl}_2$. Owing to its being soluble in water, and reacting on albuminous substances, corrosive sublimate is a strong poison. It

^{23a} Calomel (in Japanese, *keyfun*) has been prepared in Japan (and China) for many centuries, by heating mercury in clay crucibles with sea salt, which contains MgCl_2 and gives HCl . The vapour of the mercury reacts with this HCl and the oxygen of the air and forms calomel: $2\text{Hg} + 2\text{HCl} + \text{O} = 2\text{HgCl} + \text{H}_2\text{O}$. The calomel collects on the lid of the crucible in the form of a sublimate (Divers, 1894).

²⁴ HgCl_2 is partially converted into calomel even in the act of dissolving in ordinary water, especially under the action of light. The reduction of HgCl_2 into HgCl proceeds with still greater facility under the action of light in the presence of salts of oxalic acid (Shoras, 1870). According to Kistiakoffsky (1902) a double salt acts here which may be obtained by dissolving mercuric oxalate, HgC_2O_4 , in a solution of KCl , and has the composition of a double salt of HCl and $\text{C}_2\text{H}_2\text{O}_4$, with the metals K and Hg .

is used as a disinfectant, especially in surgical operations, and for preserving natural history specimens and for embalming. Corrosive sublimate combines with mercuric oxide, forming an oxychloride or basic salt,^{24a} of the composition $\text{HgCl}_2 \cdot 2\text{HgO}$ (magnesium and zinc form similar compounds). This compound is obtained by mixing a solution of corrosive sublimate with either mercuric oxide or a solution of sodium bicarbonate. In general, with both mercurous and mercuric salts, there is a marked tendency to form basic salts.²⁵

^{24a} As feebly energetic bases (like, for instance, the oxides MgO , ZnO , PbO , CuO , Al_2O_3 , Bi_2O_3 , &c.), mercuric oxide and mercurous oxide easily give basic salts, which are usually directly formed by the action of water on the normal salt, according to the general equation (for mercuric compounds, RX_2):



or else are produced directly from the normal salt and the oxide or its hydroxide. Thus mercurous nitrate, when treated with water, forms basic salts of the composition $6(\text{HgNO}_3) \cdot \text{Hg}_2\text{O} \cdot \text{H}_2\text{O}$; $2(\text{HgNO}_3) \cdot \text{Hg}_2\text{O} \cdot \text{H}_2\text{O}$, and $3(\text{HgNO}_3) \cdot \text{Hg}_2\text{O} \cdot \text{H}_2\text{O}$, the first two of which crystallise well. Our present knowledge of basic salts is not sufficiently complete to admit of generalisations. However, it is already possible to view the subject in the following aspects: (1) basic salts are principally formed from feeble bases; (2) certain metals (mentioned above) form them with particular ease, so that one of the causes of the formation of many basic salts must depend on the property of the metal itself; (3) those bases which readily form basic salts as a rule also readily form double salts; (4) in the formation of basic salts, as also everywhere in chemistry, where sufficient facts have accumulated, we clearly see the conditions of equally balanced heterogeneous systems, such as we saw, for instance, in the formation of double salts, crystallo-hydrates, &c.

The mercuric salts often form double salts, and mercuric chloride easily combines with ammonia, forming $\text{Hg}(\text{NH}_4)_2\text{Cl}_4$, or in general $\text{HgCl}_2 \cdot n\text{MCl}$. If a mixture of mercurous and potassium sulphates is dissolved in dilute sulphuric acid, the solution readily yields large colourless crystals of a double salt of the composition $\text{K}_2\text{SO}_4 \cdot 3\text{HgSO}_4 \cdot 2\text{H}_2\text{O}$. Boullay obtained crystalline compounds of mercuric chloride with hydrochloric acid, and of mercuric iodide with hydriodic acid; and Thomsen describes the compound $\text{HgBr}_2 \cdot \text{HBr} \cdot 4\text{H}_2\text{O}$ as a well-crystallised salt, melting at 13° , and having, in a molten state, a specific gravity 3.17 and a high index of refraction. Moreover, the capacity of salts for forming basic compounds has been considerably cleared up since the investigations (by Wiirtz, Lorenz, and others) of glycol, $\text{C}_2\text{H}_4(\text{OH})_2$ (and of polyatomic alcohols resembling it), because the ethers $\text{C}_2\text{H}_4\text{X}_2$, corresponding with it, are capable of forming compounds of the composition $\text{C}_2\text{H}_4\text{X}_2 \cdot n\text{C}_2\text{H}_4\text{O}$.

On the other hand, there is reason to think that the property of forming basic salts is connected with the polymerisation of bases, especially colloidal ones (see the chapters on Silica, Lead Salts, and Tungstic Acid). This still offers a vast and fruitful field for theoretical and experimental research, to which the beginner's attention ought certainly to be drawn.

²⁵ **Mercuric iodide**, HgI_2 , is obtained first as a yellow, and then as a red, precipitate on mixing solutions of mercuric salts and potassium iodide, and is soluble in an excess of the latter (in consequence of the formation of the double salt, HgKI_3) or of ammonium chloride (for a similar reason), &c. It crystallises at the ordinary temperature in square prisms of a red colour. On being heated to 126° , these change into yellow rhombic crystals, isomorphous with mercuric chloride. This yellow form of mercuric iodide is very unstable, and when cooled and triturated easily assumes the more stable red form again. When fused, a yellow liquid is obtained. This is an instance of dimorphism. After the

Mercury has a remarkable power of forming very unstable compounds with ammonia, in which the mercury replaces the hydrogen, and, if a mercuric compound be taken, its atom occupies the place of two atoms of the hydrogen in the ammonia. Thus Plantamour and Hirtzel showed that when precipitated mercuric oxide, dried at a gentle heat, is continuously heated (up to 100° – 150°) in a stream of dry ammonia, it leaves a brown powder of **mercuric nitride**, N_2Hg_3 , according to the equation: $3HgO + 2NH_3 = N_2Hg_3 + 3H_2O$.^{25a} This substance, which is attacked by water, acid, and alkalies (giving a white powder), is very explosive when struck or rubbed, and evolves nitrogen, proving that the bond between the mercury and the nitrogen is very feeble.²⁶ By the action of liquefied ammonia on yellow mercuric

addition of caustic potash, a solution of HgI_2 in KI (there is no precipitate) gives NH_4I with even traces of ammonia. This is NH_4Cl with the substitution of H_4 by Hg_2 and Cl by I , according to the equation: $2HgI + NH_3 + KHO = NH_4I + 3KI + 3H_2O$, and this reaction is employed for detecting the presence of ammonia (Nessler's test).

Mercuric cyanide, $Hg(CN)_2$, forms one of the most stable metallic cyanides. It is obtained by dissolving mercuric oxide in prussic acid, and by boiling Prussian blue with water and mercuric oxide, ferric oxide being then obtained in the precipitate. Mercuric cyanide is a colourless crystalline substance, soluble in water, and distinguished by its great stability; sulphuric acid does not liberate prussic acid from it, and even caustic potash does not remove the cyanogen (a complex salt is probably produced), but the halogen acids disengage HCN . Like the chloride, it combines with mercuric oxide, forming the oxycyanide, $Hg_2O(CN)_2$, and it shows a very marked tendency to form double compounds—for example, $K_2Hg(CN)_4$. The alkali chlorides and iodides form similar compounds—for instance, the salt $HgKI(CN)_2$ crystallises very well, and is produced by directly mixing solutions of potassium iodide and mercuric cyanide.

Wells (1889) and Vare obtained and investigated many such double salts, and showed the possibility of the formation, not only of $HgCl_2, MCl$ and $HgCl_2, 2MCl$, where M is a metal of the alkalis—for example, Cs —but also of $HgCl_2, 3MCl$, $2(HgCl_2), MCl$, and in general $nHgX_2, mMX$, where X stands for various haloids.

^{25a} See Chap. XIX., note 6a: Hg_3P_2 . In studying the metallic nitrides it is necessary to keep the corresponding phosphides in mind.

²⁶ Hg_3N_2 is similar in composition to Mg_3N_2 , &c. (Chap. XIV.). The readiness with which mercuric nitride explodes shows that the connection between the nitrogen and the mercury is very unstable, and explains the circumstance that the so-called **mercury fulminate**, or **fulminating mercury**, is an example of explosives in general. This substance is prepared in large quantities for explosive mixtures; it enters into the composition of percussion caps, which explode when struck, and ignite gunpowder. Mercury fulminate was discovered by Howard, and from that time has been prepared in the following way: one part of mercury is dissolved in twelve parts of nitric acid of sp. gr. 1.36, and when the whole of the mercury is dissolved, 5.5 parts of 90 per cent. alcohol are added, and the mass is shaken. A reaction then commences, accompanied by a rise in temperature due to the oxidation of the alcohol. As a matter of fact, many oxidation products are produced during the action of the nitric acid on the alcohol (glycollic acid, ethers, &c.). When the reaction becomes tolerably vigorous, the same quantity of alcohol is added as at the commencement, when a grey precipitate of the fulminate separates. This salt has the composition $C_2Hg(NO_2)N$. It explodes when struck or heated. The mercury in it may be replaced by other metals—for instance, copper or zinc, and also silver. The silver salt, $C_2Ag_2(NO_2)N$, is obtained in a precisely analogous manner, and is even more explosive. Under the action of alkali chlorides, only half the silver is

oxide, Weitz also obtained an explosive compound, dinmercurammonium hydroxide, N_2Hg_4O , which corresponds with an ammonium oxide, $(NH_4)_2O$, in which the whole of the hydrogen is replaced by mercury. A solution of ammonia reacts with mercuric oxide, forming the hydroxide, NHg_2OH , to which a whole series of salts, NHg_2X (see note 25), correspond; these are generally insoluble in water and capable of decomposing with an explosion. But salts of the same type, but with one atom of mercury, NH_2HgX , are more frequently and more easily formed; they were principally studied by Kane, although known much earlier. Thus, if ammonia is added to a solution of corrosive sublimate (or, still better, in reverse order), a precipitate is obtained

replaced by the alkali metal, but if the whole of the silver is replaced by an alkali metal, the salt decomposes. This is evidently because combinations of this kind proceed in virtue of the formation of substances in which mercury, and metals akin to it, are connected in an unstable way with nitrogen. Potassium and other light metals are incapable of entering into such connection, so that the substitution of potassium for mercury entails the splitting-up of the combination. Investigations of the fulminates were carried out by Gay-Lussac and Liebig, but only the investigations of L. N. Shishkoff fully cleared up the composition of these substances and their relation to the other carbon compounds. Shishkoff showed that fulminates correspond with the nitro-acid, $C_2H_2(NO_2)_2N$. The explosiveness of the group depends partly on its containing at the same time NO_2 and carbon; we already know that all such nitrogen compounds are explosive. If we imagine that the NO_2 is replaced by hydrogen, we shall have a substance of the composition C_2H_3N . This is acetonitrile—that is, acetic acid + $NH_3 - 2H_2O$, or ethenyl nitrile, as shown in Chap. VI. The formation of an acetic compound by the action of nitric acid on alcohol is easily understood, because acetic acid is produced by the oxidation of alcohol, and the production of the elements of ammonia, indispensable for the formation of a nitrile, is accounted for by the fact that nitric acid, under the action of reducing substances, in many cases forms ammonia (Chap. VI., note 27). Moreover, a certain analogy has been found between fulminating acid and hydroxylamine, but details upon this subject must be looked for in works on organic chemistry. The explosiveness of fulminating mercury, the rapidity of its decomposition (gunpowder, and even gun-cotton, burn more slowly and explode less violently), and the force of its explosion are such that a small quantity (loosely covered) will shatter massive objects.

The investigations of Abel on the communication of explosion from one substance to another are remarkable. If gun-cotton is ignited in an open space, it burns quietly; but if fulminating mercury be exploded by the side of it, the decomposition of the gun-cotton will be effected instantaneously, and it then shatters the objects upon which it lies, so rapid is the decomposition. Abel explains this by supposing that the explosion of the fulminating salt brings the molecules of gun-cotton into a uniform or as it were harmonious state of vibration, which causes the rapid decomposition of the whole mass. This rapid decomposition of explosive substances defines the distinction between explosion and combustion. Besides this, Berthelot showed that from that form of powerful molecular concussion which takes place during the explosion of fulminating mercury, the state of strain and stability of equilibrium of substances which are endothermal, or capable of decomposing with the disengagement of heat—for instance, cyanogen, nitro-compounds, nitrous oxide, &c.—is generally destroyed. Thorpe showed that carbon bisulphide, CS_2 , also an endothermal substance, decomposes into sulphur and charcoal, when fulminating mercury is exploded in contact with it. Such experiments with explosives thus offer a subject of inexhaustible interest, and, notwithstanding their danger, are eagerly prosecuted by men of science.

known as white precipitate (*Mercurius præcipitatus albus*) or **mercurammonium chloride**, NH_2HgCl , which may also be regarded not only as sal-ammoniac with the substitution of H_2 by mercury, but also as HgX_2 , where one X represents Cl and the other X represents the ammonia radicle, $\text{HgCl}_2 + 2\text{NH}_3 = \text{NH}_2\cdot\text{HgCl} + \text{NH}_4\text{Cl}$. When heated, mercurammonium chloride decomposes, yielding mercurous chloride; when heated with dry hydrochloric acid it forms ammonium chloride and mercuric chloride. Other simple and double salts of mercurammonium, NH_2HgX , are also known. Pesci (1890) showed that all the compounds HgH_2NX may be regarded as compounds of the above-named Hg_2NX with NH_4X because their sum equals $2\text{HgH}_2\text{X}$.^{26a}

Mercury as a liquid metal is capable of dissolving other metals and forming solid and liquid metallic solutions or alloys. These are generally called **amalgams**. The formation of these solutions is often accompanied by the development of a large amount of heat, for instance, when potassium and sodium are dissolved (Chap. XII., note 39); but sometimes heat is absorbed, as, for instance, when lead is dissolved. It is evident that phenomena of this kind are very similar to the phenomena accompanying the dissolution of salts and other substances in water, but here it is easy to demonstrate what is far more difficult to observe in the case of salts: the solution of metals in mercury is accompanied by the formation of definite chemical compounds of the mercury with the metals dissolved. This is shown by the fact that when pressed (best of all in chamois leather) such solutions leave solid, definite compounds of mercury with metals. It is, however, very difficult to obtain them in a pure state, on account of the difficulty of separating the last traces of mercury, which is mechanically distributed between the crystals of the compounds. Nevertheless, in many cases such compounds have undoubtedly been obtained, and their existence is clearly shown by the evident crystalline structure and characteristic appearance and fixed melting-point, which

^{26a} The capacity for replacing hydrogen in chloride of ammonium by metals also belongs to Zn and Cd. Kvasnik (1892), by the action of ammonia upon alcoholic solutions of CdCl_2 and ZnCl_2 , obtained substances of the general formula $\text{M}(\text{NH}_3\text{Cl})_2$, formed as it were from two molecules of sal-ammoniac by the substitution of two atoms of hydrogen by a diatomic metal. These substances appear as white finely crystalline powders. Under the action of heat half the ammonia passes off, and a compound of the composition $\text{MCl}\cdot\text{NH}_3\text{Cl}$ is formed.

We may further remark that in the series Mg, Zn, Cd, and Hg the capacity to form double salts of diverse composition increases with the atomic weight. Thus, according to Wells and Walden's observations (1893), the ratio $n : m$ for the type $n\text{MCl}\cdot m\text{RCl}_2$ ($\text{M} = \text{K, Li, Na} \dots \text{R} = \text{Mg, Zn} \dots$) is for Mg, 1 : 1, and for Zn, 3 : 1, 2 : 1, and 1 : 1; for Cd, in addition, salts are known with the ratio 4 : 1, and for Hg, 3 : 1, 2 : 1, 1 : 1, 2 : 3, 1 : 2, and 1 : 5.

is sometimes, as in the alloy with Na or K, higher than that of the component metals, &c. Thus, for instance, if about $2\frac{1}{2}$ per cent. of sodium is dissolved in mercury, a hard, crystalline amalgam is obtained, very friable and little changeable in air. It contains the compound NaHg_5 (Chap. XII., note 39). Water decomposes it, with the evolution of hydrogen, but more slowly than other sodium amalgams, and this action of water only shows that the bond between the sodium and the mercury is weak, just like the connection between mercury and many other elements—for instance, nitrogen. Mercury directly and easily dissolves potassium, sodium, zinc, cadmium, tin, gold, bismuth, lead, &c., and from such solutions or alloys it is in most cases easy to extract definite compounds; thus, for instance, the compounds of mercury and silver have the compositions HgAg and Ag_2Hg_3 . Objects made of copper when rubbed with mercury become covered with a white coating of that metal, which slowly forms an amalgam; silver acts in the same way, but more slowly, and platinum combines with mercury with still greater difficulty. This metal only forms an amalgam readily when in the form of a fine powder. If salts of platinum in solution are poured on to an amalgam of sodium, the latter element reduces the platinum, and the platinum separated is dissolved by the mercury. Almost all metals readily form amalgams if their solutions are decomposed by a galvanic current, where mercury forms the negative pole (cathode). In this way an amalgam may even be made with iron, although iron in mass does not dissolve in mercury. Some amalgams are found in nature—for instance, silver amalgams. Amalgams are used in considerable quantities in the arts. Thus the solubility of silver in mercury is taken advantage of for extracting that metal from the ore by means of amalgamation, and for silvering by fire. The same is the case with gold. Tin amalgam, which is incapable of crystallising and is obtained by dissolving tin in mercury, composes the brilliant coating of ordinary looking-glasses—silver is now preferred for this purpose (Chap. XXIV.)—which is made to adhere to the surface of the polished glass by simply pressing, by mechanical means, sheets of tin foil bathed in mercury on to the cleansed surface of the glass.²⁷

²⁷ I consider it appropriate here to call attention to the want of an element (ekacadmium) between cadmium and mercury in the periodic system (Chap. XV.). But as in the ninth series there is not a single known element, it may be that this series is entirely composed of elements incapable of existing under present conditions, or it may be replaced by the rare metals (Chap. XVII.). However, until this is proved in one way or another, it may be concluded that the properties of ekacadmium will be between those of cadmium and mercury. This metal ought to have an atomic weight of about 155, to form an oxide EeO and a slightly stable oxide Ee_2O . Both these ought to be feeble bases,

easily forming double and basic salts. The volume of the oxide will be approximately 17.5, because the volume of cadmium oxide is about 16, and that of mercuric oxide 19. Therefore the density of the oxide will approach $171 \div 17.5 = 9.7$. The metal ought to be easily fusible, oxidising when heated, of a grey colour, with a specific volume about 14 (cadmium = 13. mercury = 15), and, therefore, its specific gravity ($155 \div 14$) will be about 11. Such a metal is unknown. But in 1879 Dahl, in Norway, discovered in the island of Oterö, not far from Kragerö, in a vein of Iceland spar in a nickel mine, traces of a new metal which he called **norwegium**, and which presented a certain resemblance to eka-cadmium. I have not heard more about it, and possibly it is not a new element after all. A solution of the roasted mineral in acid was twice precipitated by sulphuretted hydrogen, and again ignited; the oxide obtained was easily reduced.

Amongst the metals accompanying zinc but not authentically separated, the **actinium** of Phipson (1881) might be mentioned if the information about it were more authentic and its name did not give the probability of its being confused with the actinium which possesses the radio-active properties mentioned in Chap. XXI. on Uranium.

CHAPTER XVII

BORON, ALUMINIUM, AND THE ANALOGOUS METALS OF THE THIRD GROUP

IF the elements of small atomic weight which we have hitherto discussed be placed in order, it will be clearly seen that, judging by the formulæ of their higher compounds, one element is wanting between beryllium and carbon. For lithium, $\text{Li}=7$, gives LiX , beryllium, $\text{Be}=9$, forms BeX_2 , and then comes carbon, $\text{C}=12$, giving CX_4 . Evidently to complete the series we must look for an element forming RX_3 , and having an atomic weight greater than 9 and less than 12. And such a one is **boron**; its atomic weight is 11, and its compounds are expressed by BX_3 . Lithium and beryllium are metals; carbon has no metallic properties; boron appears in a free state in several forms which are intermediate between the metals and non-metals. Lithium gives an energetic caustic oxide and beryllium forms a very feeble base; hence one would expect to find that the oxide of boron, B_2O_3 , has still more feeble basic properties and some acid properties, especially as CO_2 and N_2O_5 , which follow B_2O_3 in their composition and in the periodic system, are acid oxides. And, indeed, the only known **oxide of boron** exhibits a feeble basic character, together with the properties of a feeble acid oxide. This is even seen from the fact that a solution of boron oxide reddens blue litmus and acts on turmeric paper as an alkali, and these reactions may be used for determining the presence of B_2O_3 in solutions. By themselves the alkali borates have an alkaline reaction, which clearly indicates the feeble acid character of boric acid. If they are mixed in solution with hydrochloric acid, boric acid is liberated, and if a piece of turmeric paper is immersed in this solution and then dried, the excess of hydrochloric acid volatilises, while the boric acid remains on the paper, and communicates a **brown coloration to the turmeric**, just like alkalies.

Boron trioxide or boric anhydride enters into the composition of many minerals, either in combination with bases or in small quantities as an isomorphous admixture, not replacing acids but bases, and

most frequently alumina (Al_2O_3), for as a rule the amount of alumina present decreases as that of the boric anhydride increases. This substitution is explained by the similarity between the atomic composition of the oxides of aluminium (alumina) and boron. The subdivision of oxides into basic and acid can in no way be sharply defined, and here we meet with the most conclusive proof of the fact, for the oxides of boron and aluminium belong to the number of intermediate oxides, closely approaching the limit separating the basic from the acid oxides. Their type R_2O_3 is intermediate between those of the basic oxides, R_2O and RO , and those of the acid oxides, R_2O_5 and RO_3 . If we turn our attention to the chlorides, we remark that lithium chloride is soluble in water, is not volatile, and is not decomposed by water; the chlorides of beryllium and magnesium are more volatile, and are still decomposed by water, although not completely; whilst the chlorides of boron and aluminium are still more volatile and are decomposed by water. Thus the positions of boron and aluminium in the series of the elements are clearly defined by their atomic weights, and show us that we must not expect any new and distinct functions in these elements.

Boron was originally known in the form of sodium borate, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, or **borax**, or *tincal*, which was exported from Asia, where it is met with in solution in certain lakes of Thibet; it has also been discovered in California and Nevada, U.S.A.¹ Boric acid was afterwards found in sea water and in certain mineral springs.² Its

¹ Borax is obtained either directly from lakes, or by heating native calcium borate (see note 2) with sodium carbonate or else from the impure boric acid of Tuscany and sodium carbonate (carbonic anhydride is evolved). Borax gives supersaturated solutions with comparative ease (Gernez), and crystallises from them, both at the ordinary and higher temperatures, in octahedra, of the composition $\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$. Its sp. gr. is 1·81. But if the crystallisation proceeds in open vessels, then at temperatures below 56° , the ordinary prismatic crystallo-hydrate $\text{B}_4\text{Na}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$ is obtained. Its sp. gr. is 1·71, it effloresces in dry air at the ordinary temperature, and at 0° 100 parts of water dissolve about 3 parts of this crystallo-hydrate, at 50° , 27 parts and at 100° , 201 parts. Borax fuses when heated, loses its water, and gives an anhydrous salt, which at a red heat fuses into a mobile liquid and solidifies into a transparent amorphous *glass* (sp. gr. 2·37) which before hardening acquires the pasty condition peculiar to common molten glass. Molten borax dissolves many oxides and on solidifying acquires characteristic tints with the different oxides; thus oxide of cobalt gives a dark-blue glass, nickel a yellow, chromium a green, manganese an amethyst, uranium a bright yellow, &c. Owing to its fusibility and its property of dissolving oxides, borax is employed in soldering and brazing metals. Borax frequently enters into the composition of strass and fusible glasses, and, in general, many kinds of glass for special purposes, such as that used for making thermometers, &c., often contain the elements of borax.

² We may mention the following among the minerals which contain boron: calcium borate, $(\text{CaO})_3(\text{B}_2\text{O}_3)_4(\text{H}_2\text{O})_6$, found and extracted in Asia Minor, near Brusa; *boracite* (stassfurtite), $(\text{MgO})_6(\text{B}_2\text{O}_3)_8 \cdot \text{MgCl}_2$, at Stassfurt, in large crystals of the regular system and also amorphous masses (specific gravity 2·95), used in the arts; *ereméeffite* (Damour), AlBO_3 or $\text{Al}_2\text{O}_3 \cdot \text{B}_2\text{O}_3$, found in the Adulchalonsk mountains in

presence may be discovered by means of the green coloration it communicates to the flame of alcohol, which is capable of dissolving free boric acid.³ Many of the boron compounds employed in the arts are obtained from the impure boric acid extracted in Tuscany from the so-called fumaroles (*suffioni*). In these localities, which present the remains of volcanic action, steam mixed with nitrogen, hydrogen sulphide, small quantities of boric acid, ammonia, and other substances, issues from the earth.^{3a} The boric acid partially volatilises with the steam, for if a solution of boric acid be boiled, the distillate will always contain a certain amount of this substance.⁴

colourless transparent prisms (specific gravity 3.28) resembling apatite; *datholite* $(\text{CaO})_2(\text{SiO}_2)_2\text{B}_2\text{O}_3 \cdot \text{H}_2\text{O}$; and *ulksite*, or the boron-sodium carbonate, from which a large quantity of borax is now extracted in America (note 1). As much as 10 per cent. of boric anhydride sometimes enters into the composition of tourmaline and axinitic.

³ This green coloration is best seen by taking an alcoholic solution of volatile ethyl borate, which is easily obtained by the action of boron chloride on alcohol.

^{3a} P. Chigeffsky showed in 1884 (at Geneva) that in the evaporation of saline solutions many salts are carried off by the vapour; for instance, if a solution of potash containing about 17–20 grams of K_2CO_3 per litre be boiled, about 5 milligrams of salt are carried off for every litre of water evaporated. With Li_2CO_3 the amount of salt carried over is infinitesimal, and with Na_2CO_3 it is half that given by K_2CO_3 . The volatilisation of B_2O_3 under these circumstances is incomparably greater; for instance, when a solution containing 14 grams of B_2O_3 per litre is boiled, every litre of water evaporated carries over about 350 milligrams of B_2O_3 . When Chigeffsky passed steam through a tube containing B_2O_3 at 400° , it carried away so much of this substance that the flame of a Bunsen's burner into which the steam was led gave a distinct green coloration; but when, instead of steam, air was passed through the tube there was no coloration whatever. By placing a tube with a cold surface in steam containing B_2O_3 , Chigeffsky obtained a crystalline deposit of the hydrate $\text{B}(\text{OH})_3$ on the surface of the tube. Besides this, he found that the amount of B_2O_3 carried over by steam increases with the temperature, and that crystals of $\text{B}(\text{OH})_3$ placed in an atmosphere of steam (although perfectly still) volatilise, showing that this is not a matter of mechanical transfer, but is based on the capacity of B_2O_3 and $\text{B}(\text{OH})_3$ to pass into a state of vapour in an atmosphere of steam.

⁴ How it is that these vapours containing boric acid are formed in the interior of the earth is at present unknown. Dumas supposes that it depends on the presence of **boron sulphide**, B_2S_3 (others think boron nitride), at a certain depth in the earth. This substance may be artificially prepared by heating a mixture of boric acid and charcoal in a stream of carbon bisulphide vapour, or by the direct combination of boron and the vapour of sulphur at a white heat. The almost non-crystalline compound B_2S_3 , sp. gr. 1.55, thus obtained is somewhat volatile, has an unpleasant smell, and is very easily decomposed by water, forming boric acid and hydrogen sulphide, $\text{B}_2\text{S}_3 + 3\text{H}_2\text{O} = \text{B}_2\text{O}_3 + 3\text{H}_2\text{S}$. It is supposed that a bed of boron sulphide lying at a certain depth below the surface of the earth comes into contact with sea water which has percolated through the upper strata, becomes very hot, and gives steam, hydrogen sulphide, and boric acid. The amount of boric anhydride in the vapours which escape from the Tuscan fumaroles and *suffioni* is very inconsiderable—less than one-tenth per cent.—so that the direct extraction of the acid would be very uneconomical; for this reason the heat contained in the discharged vapours is made use of for evaporating the water. This is done in the following manner: Reservoirs are constructed over the crevices evolving the vapours and the water of some neighbouring spring is passed into them. The vapours are caused to pass through these reservoirs, and in so doing they give up all their boric acid

If boric acid is introduced into an excess of a strong hot solution of sodium hydroxide, on slowly cooling, the salt $\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$ crystallises out. This salt contains an equivalent of Na_2O to one equivalent of B_2O_3 . It might be termed a neutral salt did it not possess strongly alkaline reactions and split up easily into alkali and the more stable borax or baborate of sodium mentioned above, which contains $2\text{B}_2\text{O}_3$ to Na_2O .⁵ This salt is prepared by the action of boric acid

to the water and heat it, so that after about twenty-four hours it even boils; in this way, however, only a very weak solution of boric acid is obtained. This solution is then passed into lower basins and again saturated by the vapours discharged from the earth, by which means a certain amount of the water is evaporated and a fresh quantity of



FIG. 91.—Extraction of boric acid from the fumaroles of Tuscany.

boric acid absorbed; the same process is repeated in other reservoirs until the water has collected a somewhat considerable amount of boric acid. The solution is drawn from the last reservoir, A, into settling vessels, B, D, and then into a series of vessels, a, b, c. In these vessels, which are made of lead, the solution is also evaporated by the vapours escaping from the earth, and attains a density of 10° to 11° Baumé.

⁵ Metals, like Na, K, Li, give salts of the types MBO_2 or MH_2BO_3 . A solution of borax, $\text{Na}_2\text{B}_4\text{O}_7$, has an alkaline reaction, decomposes ammonium salts with the liberation of ammonia (Bolley), absorbs carbonic anhydride, and dissolves iodine like an alkali (Georgiewics), and seems to be decomposed by water. Thus Roso showed that strong solutions of borax give a precipitate of silver borate with silver nitrate, whilst dilute solutions precipitate silver oxide, like an alkali. Georgiewics showed (1888) that all acids, acting on a mixture of solutions of potassium iodide and iodate, evolve iodine, but boric acid does not do this. With dilute solutions of sodium hydroxide Berthelot obtained a development of heat equal to $11\frac{1}{2}$ thousand calories per equivalent of alkali (40 grams of sodium hydroxide) when the ratio was $\text{Na}_2\text{O} : 2\text{B}_2\text{O}_3$ (as in borax) and only

on a solution of sodium carbonate. Borax may be perfectly purified by crystallisation, the crystals usually containing $\text{Na}_2\text{O} + 2\text{B}_2\text{O}_3 + 10\text{H}_2\text{O} = \text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$. If a saturated and hot solution of borax is mixed with strong hydrochloric acid, common salt and a normal crystalline hydrate of boric acid $\text{B}(\text{OH})_3$, having the composition $\text{B}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, are formed. The hydrate is only slightly (about 3 per cent.) soluble in water. This is the easiest method of obtaining boric acid. The water is easily expelled from this hydrate, one half being lost at 100° and the remainder on further heating, and the remaining B_2O_3 or boric anhydride fuses at 580° (according to Carnelley), forming at first a ductile (easily drawn out into threads) tenacious mass and then a colourless liquid solidifying to a transparent glass, which absorbs moisture from the atmosphere and then becomes cloudy.⁶ Only the alkaline salts of boric acid are soluble in water, but all borates are soluble in acids, owing to their easy decomposability and the solubility of boric acid itself. Although boric anhydride, B_2O_3 , absorbs $3\text{H}_2\text{O}$ from damp air, still in the presence of water it always⁷ combines with

4 thousand calories when it was $\text{Na}_2\text{O} : \text{B}_2\text{O}_3$, from which he concludes that water powerfully decomposes those sodium borates in which there is more alkali than in borax. Lanrent (1849) obtained a sodium compound, $\text{Na}_2\text{O} \cdot 4\text{B}_2\text{O}_3 \cdot 10\text{H}_2\text{O}$, containing twice as much boric anhydride as borax, by boiling a mixture of borax with an equivalent quantity of sal-ammoniac until the evolution of ammonia entirely ceased.

Hence it is evident that feeble acids are prone to form acid salts (that is, salts containing much acid oxide) as readily as feeble bases give basic salts. These relations become still clearer on an acquaintance with such feeble acids as silicic, molybdic, &c. This variety of the proportions in which bases are able to form salts recalls exactly the variety of the proportions in which water combines with crystallo-hydrates.

With respect to the feeble acid energy of boric anhydride I think it useful to add the following remarks. Carbonic anhydride is absorbed by a solution of borax, and displaces boric anhydride; but it is also displaced by it, not only on fusion, but also on solution, as the preparation of borax itself shows. Sulphuric anhydride is absorbed by boric acid, forming a compound $\text{B}(\text{HSO}_4)_3$, where HSO_4 is the radicle of sulphuric acid (D'Ally). With phosphoric acid, boric acid forms a stable compound, BPO_4 , or $\text{B}_2\text{O}_3 \cdot \text{P}_2\text{O}_5$, undecomposable by water, as Gustavson and others have shown. With respect to tartaric acid, boric anhydride is able to play the same part as antimonious oxide. Mannitol, glycerol, and similar polyhydric alcohols also form particularly characteristic compounds with boric anhydride.

⁶ Ditte determined the sp. gr. :—

	0°	12°	80°
B_2O_3	1.8766	1.8476	1.6988
$\text{B}(\text{OH})_3$	1.5463	1.5172	1.3828
Solubility	1.95	2.92	16.82

The last line gives the solubility, in grams, of boric acid, $\text{B}(\text{OH})_3$, per 100 c.c. of water, also according to the determinations of Ditte.

⁷ It is evident that, in the presence of basic oxides, water competes with them, which fact in all probability determines both the amount of water in the salts of boric acid as well as their decomposition by an excess of water. In confirmation of the above-mentioned competing action between water and bases, I think it useful to point out that the crystallo-hydrate of borax containing $5\text{H}_2\text{O}$ may be represented as $\text{B}(\text{HO})_3$, or

a small quantity of bases. Fused boric anhydride forms a crystalline compound $(\text{MgO})_3\text{B}_2\text{O}_3$ (Ebelmann) with magnesia of the same type as the hydrate, and even with soda it forms $(\text{Na}_2\text{O})_3\text{B}_2\text{O}_3$ or Na_3BO_3 (Benedict). Generally, vitreous fluxes are formed by this means,⁸ and these, when fused, recall ordinary aqueous solutions in many respects. Some of them crystallise on solidifying, and such have, like salts, a definite composition. The property of boric anhydride of forming higher grades of combination with basic oxides when fused explains the power of fused borax to dissolve metallic oxides, and the experiments of Ebelmann on the preparation of artificial crystals of the precious stones by means of boric anhydride. Boric anhydride is, although with difficulty, volatile at a high temperature, and therefore if it dissolves an oxide, it may be partially driven off from such a solution by prolonged and powerful ignition; in which case the oxide previously in solution separates out in a crystalline form, and frequently in the same form as that in which it occurs in nature; for example, crystals of alumina, which by itself fuses with difficulty, have been obtained in this manner. It dissolves in molten boric anhydride, and separates out in natural rhombohedric crystals. In this way Ebelmann also obtained *spinel*, a compound of magnesium and aluminium oxides which occurs in nature.⁹

rather as $\text{B}_2(\text{OH})_5$, with the substitution of one atom of hydrogen by sodium, since $\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O} = 2\text{B}_2(\text{OH})_5(\text{ONa})$. The composition of the acid boric salts is very varied, as is seen from the fact that Reychler (1893) obtained $(\text{Cs}_2\text{O})_3\text{B}_2\text{O}_3$, $(\text{Rb}_2\text{O})_2\text{B}_2\text{O}_3$ (corresponding to borax) and $(\text{Li}_2\text{O})_2\text{B}_2\text{O}_3$, and that Le Chatelier and Ditte obtained, for CaO , MgO , &c., $(\text{RO})\text{B}_2\text{O}_3$, $(\text{RO})_2\text{B}_2\text{O}_3$, $(\text{RO})_3\text{B}_2\text{O}_3$, and even $(\text{RO})_5\text{B}_2\text{O}_3$.

⁸ A glass can only be formed by those slightly volatile oxides corresponding with feeble acids, like silica, phosphoric and boric anhydrides, &c., which themselves give glassy masses, like quartz, glacial phosphoric acid, and boric anhydride. They are able, like aqueous solutions and like metallic alloys, either to solidify in an amorphous form or to yield (or even be wholly converted into) definite crystalline compounds. This view illustrates the position of solutions among other chemical compounds, and allows all alloys to be regarded from the point of view of the common laws of chemical reactions. I have therefore frequently resorted to it in this work, and have since the year 1850 introduced it into various provinces of chemistry.

⁹ Although boric acid in aqueous solution proves to be exceedingly feeble and un-energetic, and to be easily displaced from its salts by other acids, yet in an anhydrous state, as anhydride, it exhibits the properties of an energetic acid oxide, and **displaces the anhydrides of other acids**. This of course does not mean that the acid then acquires new chemical properties, but depends only on the fact that the anhydrides of the majority of acids are much more volatile than boric anhydride, and therefore the salts of many acids—even of sulphuric acid—are decomposed when fused with boric anhydride.

By itself boric acid is used in the arts in small quantity, chiefly for the preservation of meat and fish (which must be afterwards well washed in water) and of milk, and for soaking the wicks of stearin candles. The latter application is based on the fact that the wicks, which are made of cotton twist, contain an ash which is infusible by itself, but which fuses when mixed with boric acid.

Free **boron** was obtained (1809) by Davy, Gay-Lussac, and Thénard when they obtained the metals of the alkalis, for when boric anhydride is fused with sodium it gives up its oxygen to the sodium, and free boron is liberated as an **amorphous** powder resembling charcoal.¹⁰ It is of a brown colour, specific gravity 2.45 (Moissan), and when dry does not alter in the air at the ordinary temperature; but it burns when ignited to 700°, and in so doing combines not only with the oxygen of the air, but also with the nitrogen. However, the combustion is never complete, because the boric anhydride formed on the surface fuses and covers the remaining mass of the boron, and so preserves it from the action of the oxygen. Acids, even sulphuric (forming SO₂) and phosphoric (forming phosphorus), easily oxidise amorphous boron, especially when heated, converting it into boric acid. Alkalies have the same action on it, only in this case hydrogen is evolved. Boron decomposes steam at a red heat, also with evolution of hydrogen.

Amorphous boron, like charcoal, dissolves in certain molten metals. The property of fused **aluminium of dissolving boron** in considerable quantity is very striking; on cooling such a solution, the boron partially combined with the aluminium separates out in a crystalline form, and its properties are then exceedingly remarkable. The crystalline boron may be obtained by heating (to 1300°) the pulverulent boron with aluminium in a well-closed crucible, the access of air being prevented as far as possible. After cooling, crystals are observed

¹⁰ **Amorphous boron** is prepared by mixing 100 parts of powdered boric anhydride with 50 parts of sodium in small lumps; this mixture is thrown into a powerfully heated cast-iron crucible, covered with a layer of ignited salt, and the crucible covered. Reaction proceeds rapidly; the mass is stirred with an iron rod, and poured directly into water containing hydrochloric acid. The action is naturally accompanied by the formation of sodium borate, which is dissolved, together with the salt, by the water, whilst the boron settles at the bottom of the vessel as an insoluble powder. It is washed in water, and dried at the ordinary temperature. Magnesium, and even charcoal and phosphorus, are also able to reduce boron from its oxide. Boron, in the form of an amorphous powder, very easily passes through filter-paper, remains suspended in water, and colours it brown, so that it appears to be soluble in water. Sulphur precipitated from solutions shows the same (colloidal) property. When borax is fused with magnesium powder, it gives a brown pulverulent compound of boron and magnesium, Mg₂B (Winkler, 1890); but when a mixture of 1 part of magnesium and 3 parts of B₂O₃ is heated to redness (Moissan 1892), it yields amorphous boron in the form of a chestnut-coloured powder, which, after being washed with water, hydrochloric and hydrofluoric acids, is again fused with B₂O in an atmosphere of hydrogen in order to prevent the access of the nitrogen of the air, which is easily absorbed by incandescent amorphous boron.

Sabatier (1891) considers that a certain amount of gaseous hydride of boron is evolved in the action of hydrochloric acid upon the alloys of magnesium and boron, because the gas disengaged burns with a green flame. Still, the existence of hydride of boron cannot be regarded as certain. However, according to Winkler, a solid compound of boron and hydrogen exists, although it has not yet been obtained in a pure state.

Under the action of the heat of the electric furnace, boron forms with carbon a *carbide*, BC, as was shown by Mühlhäuser and Moissan in 1893.

on the surface of the aluminium, and may easily be separated by dissolving the latter in hydrochloric acid, which does not act on the crystals. The specific gravity of the latter is 2.68; they are partially transparent, but for the most part are coloured dark brown; they contain about 4 per cent. of carbon and up to 7 per cent. of aluminium, so that they cannot be considered as pure boron. Nevertheless, the properties of this **crystalline** substance, which was obtained by Wöhler and Deville, are very remarkable. It most closely resembles the **diamond in its properties**; in fact, these crystals have the lustre and high refracting power proper to the diamond only, whilst their hardness competes with that of the diamond. Their powder polishes even the diamond, and like the diamond scratches the sapphire and corundum. Crystalline boron is much more stable with respect to chemical reagents than the amorphous variety, and just as it resembles the diamond, so amorphous boron, on the other hand, distinctly recalls certain of the properties of charcoal; thus a certain resemblance exists between boron and carbon in a free state, which is further justified by the proximity of their positions in the periodic systems.

Among the other compounds of boron, those with nitrogen and the halogens are the most remarkable. As already mentioned above, amorphous boron combines directly with **nitrogen** at a red heat. If it is heated in a glass tube in a stream of nitric oxide, perfect combustion takes place: $5\text{B} + 3\text{NO} = \text{B}_2\text{O}_3 + 3\text{BN}$. If the residue is treated with nitric acid, the boric anhydride dissolves, whilst the boron nitride remains¹¹ as an extremely light white powder, which is sometimes partially crystalline and greasy to the touch, like talc. It is infusible and remains unchanged even at the melting-point of nickel. In general, it is remarkable for its great stability with respect to chemical reagents. Nitric and hydrochloric acids, as well as alkaline solutions, and hydrogen and chlorine at a red heat, have no action on it. When fused with potash, it evolves ammonia, and when ignited in steam it also yields ammonia: $2\text{BN} + 3\text{H}_2\text{O} = \text{B}_2\text{O}_3 + 2\text{NH}_3$.¹²

¹¹ At first boron nitride was obtained by heating boric acid with potassium cyanide or other cyanogen compounds. It may be more simply prepared by heating anhydrous borax with potassium ferrocyanide, or by heating borax with ammonium chloride. For this purpose one part of borax is intimately mixed with two parts of dry ammonium chloride, and the mixture heated in a platinum crucible. A porous mass is formed, which, after crushing and treating with water and hydrochloric acid, leaves boron nitride.

¹² When fused with potassium carbonate it forms potassium cyanate, $\text{BN} + \text{K}_2\text{CO}_3 = \text{KBO}_2 + \text{KCNO}$. All this shows that boron nitride is a nitrile of boric acid, $\text{BO}(\text{OH}) + \text{NH}_3 - 2\text{H}_2\text{O} = \text{BN}$. The same is expressed by saying that boron nitride is a compound of the type of the boron compounds BX_3 , with the substitution of X_3 by nitrogen, as the trivalent radicle of ammonia, NH_3 . *Boron phosphide*, BP, corresponding with BN, was prepared by Besson and Moissan (1891). The action of phosphorus on boron iodide, BI_3 ,

No less remarkable is the compound of boron with fluorine—**boron fluoride**, BF_3 . It is produced in many instances when a compound of boron and one of fluorine are brought together.¹³ The most convenient method of preparing it is by heating a mixture of calcium fluoride with boric anhydride and sulphuric acid: $3\text{CaF}_2 + \text{B}_2\text{O}_3 + 3\text{H}_2\text{SO}_4 = 3\text{CaSO}_4 + 3\text{H}_2\text{O} + 2\text{BF}_3$.¹⁴ It is a colourless liquefiable *gas* (the liquid boils at -100°), which on coming into contact with damp air forms white fumes owing to its combining with water. One volume of water dissolves as much as 1,050 volumes of this gas (Bazaroff), forming a liquid which disengages boron fluoride when heated, and distils over unaltered. Boron fluoride chars organic matter, owing to its taking up the water from it, and in this respect it acts like sulphuric acid. The behaviour of boron fluoride with water must be understood as a reversible reaction, since with water it yields hydrofluoric and boric acids, whilst they, acting on one another, re-form boron fluoride and water. A state of equilibrium is set up between these four substances (and between two reversible reactions) which is distinctly dependent on the mass of the water.^{14a} When boron fluoride is in great excess, the equilibrated system, which is capable of distilling over (sp. gr. of the liquid, 1.77), has a composition $\text{BF}_3, 2\text{H}_2\text{O}$, (or $\text{B}_2\text{O}_3, \text{H}_2\text{O}, 6\text{HF}$). It has also its corresponding salts.¹⁵ It is a caustic liquid, having the properties of a powerful acid; but it does not act on glass, which shows

yields PBI_3 , and this, when heated to 500° in hydrogen, gives BP, which with fused potassium hydroxide gives rise to PH_3 .

¹³ Boron fluoride is frequently evolved on heating certain compounds occurring in nature containing both boron and fluorine. If calcium fluoride is heated with boric anhydride, calcium borate and boron and fluorine are formed, and the latter, as a gas, is volatilised: $2\text{B}_2\text{O}_3 + 3\text{CaF}_2 = 2\text{BF}_3 + \text{Ca}_3\text{B}_2\text{O}_6$. The calcium borate, however, retains a certain amount of calcium fluoride.

¹⁴ In order to avoid the formation of silicon fluoride the decomposition should not be carried on in glass vessels, which contain silica, but in a lead or platinum vessel. Boron fluoride by itself does not corrode glass, but the hydrofluoric acid liberated in the reaction may bring a part of the silica into reaction. Boron fluoride should be collected over mercury, since water acts on it, as we shall see later.

^{14a} It appears to me that from this point of view it is possible to understand the apparently contradictory results of different investigators, especially those of Gay-Lussac (and Thénard), Davy, Berzelius, and Bazaroff. From the form in which the reaction of BF_3 on water is given here, it is evident that the act of solution in water is accompanied by complex chemical transformations, and I think that this example again proves the justness of those observations upon the nature of solutions given in Chap. I.

¹⁵ They are called fluoborates. They may be prepared directly from fluorides and borates. Such compounds of halogens with oxygen salts are known in nature (for instance, apatite and boracite), and may be artificially prepared. The composition of the fluoborates—for example, $\text{K}_4\text{BF}_3\text{O}_2$ —may be expressed as that of a double salt, $\text{BO}(\text{OK}), 3\text{KF}$. Although an excess of water decomposes them (Bazaroff), this does not prove that they do not exist as such, for many double salts are decomposed by water.

that there is no free hydrofluoric acid present. Under the action of water this system changes, with the formation of boric acid and hydrofluoboric acid (HBF_4), according to the equation: $4\text{BF}_3\cdot\text{H}_2\text{O} = 3\text{HBF}_4 + \text{BH}_3\text{O}_3 + 5\text{H}_2\text{O}$.¹⁶ This hydrofluoboric acid has its corresponding salts—for instance, KBF_4 . On evaporating the aqueous solution of the free acid it decomposes, with the evolution of hydrofluoric acid, and a stable system is again obtained: $2\text{HBF}_4 + 5\text{H}_2\text{O} = \text{B}_2\text{F}_6\cdot\text{H}_{10}\text{O}_5 + 2\text{HF}$. The resultant solution (containing $2\text{BF}_3\cdot 5\text{H}_2\text{O}$, sp. gr. 1.58), which is identical with that formed by the evaporation of a solution of boric acid with hydrofluoric acid, again only contains a compound of boron fluoride with water. Probably there are various other possible and more or less stable states of equilibrium and definite compounds of boron fluoride, hydrofluoric acid, and water.

Nothing of this kind occurs with boron chloride, because hydrochloric acid does not act on boric acid. However, at 400° amorphous boron burns in chlorine, and at 410° forms **boron chloride**, BCl_3 , obtained as a gas which, in a freezing mixture, condenses into a liquid boiling at 17° , and gives up its excess of chlorine, if there be any, to mercury. The specific gravity of this liquid is 1.42 at 6° . Boron chloride may also be directly obtained from boric anhydride by the simultaneous action of charcoal and chlorine at a high temperature; $\text{B}_2\text{O}_3 + 3\text{C} + 3\text{Cl}_2 = 2\text{BCl}_3 + 3\text{CO}$. It is also obtained by the action of phosphoric chloride on boric anhydride in a closed tube at 200° . It is completely decomposed by water, like the chloranhydride of an acid, boric acid being formed; hence it fumes in the air: $2\text{BCl}_3 + 6\text{H}_2\text{O} = 2\text{BH}_3\text{O}_3 + 6\text{HCl}$. Boron forms with bromine a similar compound, BBr_3 , having the specific gravity 2.64 at 6° and boiling at 90° . The vapour densities of the fluoride, chloride, and bromide of boron show that they contain three atoms of the halogen in the molecule—that is, that boron is a trivalent element forming BX_3 .^{16a}

As in the first group lithium is followed by sodium, giving a more basic oxide, so in the second group beryllium is followed by magnesium,

¹⁶ Fluoboric acid contains boron fluoride and water; hydrofluoboric acid, boron fluoride, and hydrofluoric acid. It is evident that on the one side the competition between water and hydrofluoric acid, and, on the other hand, their power to combine, are among the forces which act here. From the fact that hydroborofluoric acid, HBF_4 , can only exist in an aqueous solution, it must be assumed that it forms a somewhat stable system only in the presence of $3\text{H}_2\text{O}$.

^{16a} Iodide of boron, BI_3 , was obtained by Moissan (1891), by heating a mixture of the vapours of HI and BCl_3 in a tube, or by the action of iodine vapour (at 750°) or HI upon amorphous boron. BI_3 is a solid substance which dissolves in benzene and CS_2 , reacts with water, melts at 43° , boils at 210° , has a density 3.3 at 50° , and partially decomposes in the light. Besson (1891) obtained BIBr_2 (boiling at 125°) and BI_2Br (boiling at 180°) by heating 300° – 400° a mixture of the vapours of HI and BBr_3 , and he showed also that NH_3 combines with BBr_3 and BI_3 in various proportions.

and so also in the third group there is, besides the lightest element, boron, whose basic character is scarcely defined, **aluminium**, $\text{Al}=27$, the oxide of which, alumina, has somewhat distinct basic properties, not so powerful as in magnesium oxide, but more distinct than in boric anhydride. Of the elements of the third group, aluminium is the most widely distributed in nature; it will be sufficient to mention that it enters into the composition of clay to demonstrate the universal distribution of aluminium in the earth's crust. Aluminium is so named from its being the metal of alums (*alumen*). **Clay**, which is so widely distributed and familiar to everybody, is the insoluble residue obtained after the action of water containing carbonic acid on many rocks, and especially on the felspars contained in some of them. Felspar is a compound containing potash or soda, alumina, and silica. The primary rocks, like granite, contain many similar compounds (see Chap. XVIII.: Felspars). Felspar is acted on by water containing carbonic acid, all the alkalies (potash and soda) and a portion of the silica passing into the water as substances which are soluble and carried away by it, whilst the alumina and silica left from the felspar remain on the spot where the solution has taken place. This is the original method of the formation of clay in its primary deposits among rocks along the crevices of which the atmospheric water has permeated. Such primary deposits often contain a white pure clay, termed **kaolin** or **porcelain clay**. But such clay is a rarity, because the conditions for its formation are seldom met with. The water, while acting chemically on rocks, at the same time destroys them *mechanically*, and carries off the finely divided residues of disintegration with it. Clay is most easily subjected to this mechanical action of water, because it is composed of grains of exceedingly small size and void of any visible crystalline structure, which readily remain suspended in water. The cloudy water of running mountain streams generally contains suspended particles of clay, formed by the above-described chemical and mechanical action of the water on the minerals contained in the mountain rocks. Together with these minute particles of clay the water carries away the coarser components on which it is not able to act—for example, splinters of rock, grains of mica, quartz, &c. They were originally held together by those minerals which form clay. When the water acts on these binding minerals, a sandy mass is formed which water bears away. The cloudy water in which the particles of clay and sand are held in suspension carries them to, and deposits them at, the estuaries of rivers, lakes, seas, and oceans. The coarser particles are first deposited and form sand and similar disintegrated rocky matter, whilst the clay, owing to its finely divided state, is carried on further, and is

only deposited in the still parts of the rivers, lakes, &c. Such disintegration of rocks and separation of clay from sand has been gradually going on during the millions of years of the earth's existence, and is now proceeding, and has been the cause of the formation of immense deposits of sandstone and clay. Beds of clay may have been transferred by currents and streams from one locality to another, so that we must distinguish between primary and secondary deposits of clay. In some places these beds of clay have, owing to long exposure under water, and partially owing to the action of heat, undergone compression, and have formed the rocky masses known as clay slates and schists, which sometimes form entire mountains. Roofing slates belong to this class of rocks.

From what has been said above it will be evident that these deposits can never consist of a chemically pure and homogeneous substance, but will contain all kinds of extraneous, insoluble, finely divided matter, and especially sand—that is, fragments of rock, chiefly quartz (SiO_2). It is, however, possible to considerably purify clay from these impurities, owing to the fact that they are the result of mechanical disintegration, whilst the clay has been formed as a residue of the chemical alteration of rocky matter, and therefore its particles are incomparably more minute than the particles of sand and other rock fragments mixed with it. This difference in the size of the grains causes the clay to remain longer in suspension than the coarser grains of sand, when shaken up in water. If clay be shaken up in water, and especially if it be previously boiled in it, and if after the first portion has settled the cloudy water be decanted, it will give a deposit of a very much purer clay than the original. This method is employed for purifying kaolin designed for the manufacture of the best kinds of china, earthenware, &c. A similar method is also employed in the investigation of earths for determining the **composition of soils**, which are chiefly composed of a mixture of sand, clay, limestone, and mould. The limestone is soluble in dilute acids, but neither the clay nor sand passes into solution by this means, and therefore the limestone is easily separated in the investigation of soils. The clay is separated from the sand by a mechanical method similar to that described above, and termed *levigation*.¹⁷

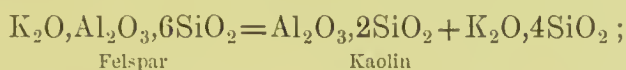
¹⁷ The process of **levigation** is based on the difference in the diameters of the particles of clay and sand. In density these particles differ but little from each other, and a stream of water of a certain velocity can only carry away the particles of a certain diameter, whilst the particles of a larger diameter cannot be borne away by it. This is due to the resistance to falling offered by the water. This resistance to substances moving in it increases with the velocity, and therefore a substance falling into water will only move with an increasing velocity until its weight equals the resistance offered by

By treating clay with strong sulphuric acid, which dissolves the alumina in it, and then (by means of an alkaline carbonate) dissolving the

the water, and then the velocity will be uniform. And as the weight of the minute particles of clay is small, the maximum velocity attained by them in falling is also small. (A detailed account of the theory of bodies falling in liquids, and of the experiments bearing on this subject, may be found in my work, *Concerning the Resistance of Liquids and Aeronautics*, 1880.) The minute particles of clay remain suspended longer in water, and take longer to fall to the bottom. Heavy particles, although of small dimensions, fall more quickly, and are borne away by water with greater difficulty than the lighter. In this way gold and other heavy ores are washed free from sand and clay, and the coarser portions and heavier particles are left behind. A current of water of a certain velocity cannot carry away with it particles of more than a definite diameter and density, but by increasing the velocity of the current a point may be arrived at when it will bear away larger particles. A description of apparatus for the observation of phenomena of this kind is given by Schöne in his memoir in the *Transactions of the Moscow Society of Natural Sciences* for 1867. In order to be able to vary accurately the velocity of the current of water, a cylinder is employed in which the earth to be experimented on is placed, and water is introduced through the conical bottom of the cylinder. The rate at which the water rises in the cylinder will vary according to the quantity of water flowing per unit of time into the vessel, and consequently particles of various sizes will be carried away by the water flowing over the upper edges of the vessel. Schöne showed by direct experiment that a current of water having a velocity of 0.1 mm. per second will carry away particles of earth having a diameter of not more than 0.0075 mm., that is, only the most minute; with a velocity $v=0.2$ mm. per second, particles having a diameter $d=0.011$ mm. are carried away; with $v=0.3$ mm., $d=0.0146$ mm.; with $v=0.4$ mm., $d=0.017$ mm.; with $v=0.5$ mm., $d=0.02$ mm.; with $v=1$ mm., $d=0.03$ mm.; with $v=4$ mm., $d=0.07$ mm.; with $v=10$ mm., $d=0.137$ mm.; with $v=12$ mm., $d=0.15$ mm.; and therefore if the current does not exceed one of these velocities, it will only carry or wash away particles having a diameter less than that indicated. The sand and other particles mixed with the clay will then remain in the vessel. The very minute particles obtained after levigation are all considered as clay, although not only clay but other rock residue may also exist in it as very fine particles. However, this is very seldom the case, and the fine mud separated from all clays has practically the same composition as the purest kinds of kaolin.

The relation between the amounts of clay and sand in soils used for the cultivation of plants is very important, because a soil rich in clay is denser and heavier and shrinks up under the action of heat, and does not readily yield to the plough in very dry or wet weather, whilst a rich soil in sand is friable and crumbling, easily parts with its moisture, and dries rapidly, but is comparatively easily worked. Neither crumbling sand nor pure clay can be regarded as a good cultivating soil. The difference in the amounts of clay and sand in a soil has also a purely chemical signification. Sand is easily permeated by the air, because its particles are not closely packed together. Hence the chemical change of manures proceeds very easily in sandy soils. But on the other hand such soils do not retain the nutritious principles contained in the manure, nor the water necessary for the nourishment of plants by means of their roots, and are much injured by drought. Solutions of nutritious substances, containing salts of potassium, phosphoric acid, &c., when passed through sand only leave a portion moistening the surface of its particles. The sand has only to be washed with pure water, and all the adhering films of solution are washed away. It is not so with clay. If the above solutions be passed through a layer of clay, the retention of the nutritive substances of these solutions will be very marked; this is partly because of the very large surface which the minute particles of clay expose. The nutritive elements dissolved in water are retained by the particles of clay in a peculiar manner—that is, the absorptive power of clay is very great compared with that of sand—and this has a great significance in the economy of nature (Chap. XIII.). It is

silica which was combined with the alumina in the clay (but not that occurring in the form of sand, &c., which is hardly dissolved by carbonate of soda solution at all even on boiling), we may form an idea of the proportion between the component parts of a clay; and by igniting it at a high temperature we may determine the amount of water held in it. In the purer sorts of clay dried at 100° (sp. gr. of pure kaolin is about 2.5) this proportion is about $2\text{SiO}_2 : 2\text{H}_2\text{O} : \text{Al}_2\text{O}_3$. In this case the conversion of felspar into kaolin is expressed by the equation:



the compound $\text{K}_2\text{O}, 4\text{SiO}_2$ passes into solution.

evident that for cultivation the most convenient soils in every respect will be those containing a definite mixture of clay and sand, and indeed the most fertile soils have such a composition. The study of fertile soils, which is so important for a knowledge of the natural conditions for the application of fertilisers, belongs, strictly speaking, to the province of agriculture. In Russia the first foundation of scientific fertilisation has been laid by Prof. V. V. Dokuchaeff. As an example only, we shall give the composition of four soils: (1) The black earth of the Simbirsk government; (2) a clay soil from the Smolensk government; (3) a more sandy soil from the Moscow government; and (4) a peaty soil from near St. Petersburg. These analyses were made in the laboratory of the St. Petersburg University about 1860, in connection with experiments on fertilisation (conducted by me) by the Imperial Free Economical Society. Ten thousand grams of air-dried soil contain the following quantities (in grams) of substances capable of dissolving in acids, and of serving for the nourishments of plants.

	(1)	(2)	(3)	(4)
Na_2O	11	5	4	4
K_2O	58	10	7	5
MgO	92	33	19	7
CaO	134	17	14	11
P_2O_5	7	1	7	3
N	44	11	13	16
S	13	7	7	6
Fe_2O_3	341	155	111	46

By chemical and mechanical analysis, the chief component parts per 100 parts of the four air-dried soils were found to be:—

Clay	46	29	12	10
Sand	40	67	86	84
Organic matter	3.7	1.7	0.6	4.1
Hygroscopic water	6.3	1.3	0.8	1.9
Weight of a litre in grams	1150	1270	1350	960

The black earth excels the other soils in many respects, but naturally its stores are also exhausted by cultivation if nothing is returned to it in the form of fertilisers; and the improvement of a soil (for instance, by the addition of marl or peat, and by drainage and watering), and its fertilisation, if carried on in conformity with its composition and with the properties of the plants to be cultivated, are capable of rendering not only every soil fit for cultivation, but also of improving its value, so that in the course of time whole countries (like Holland) may clearly improve their agricultural position, whilst under the ordinary *régime* of continued exhaustion of the soil, entire regions (as, for instance, many parts of Central Asia) may be rendered unfit for any agriculture.

But as a rule clays contain from 45 to 60 per cent. of silica, from 20 to 30 of alumina, and about 12 of water; and it cannot be supposed that clays are always homogeneous, because they are an aggregation of residues (of silico-aluminous compounds) which are unacted on by water. Nevertheless, clays always contain a hydrated compound of alumina and silica, which is able to give up the alumina contained by it as a base to strong sulphuric acid, forming aluminium sulphate, which is soluble in water. After this treatment the silica remains, and is soluble in a solution of an alkaline carbonate.¹⁸

Clay is the source from which alumina, Al_2O_3 , and the majority of the compounds of aluminium are prepared. Among these compounds the most important are the alums—that is, the double sulphates of potassium (and allied metals) and aluminium, $\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$. When clay is treated with sulphuric acid diluted with a certain amount of water, aluminium sulphate, $\text{Al}_2(\text{SO}_4)_3$, is formed; and if potassium carbonate or sulphate is added to this solution, a double salt or alum is obtained in solution. The alums crystallise easily, and are prepared on a very large manufacturing scale owing to their being employed in the process of dyeing. Alums are soluble in water, and, on the addition of ammonia to their solutions, they give hydrated

¹⁸ Everyone knows that a mixture of clay and water is endowed with the property of taking a given form when subjected to a moderate pressure. This plasticity of clay renders it an invaluable material for practical purposes. From clay are moulded and manufactured a variety of objects, beginning with the common brick and ending with the most delicate china works of art. This **plasticity of clay** increases with its purity. When articles made of clay are dried, the well-known hard mass is obtained; but water washes it away, and, furthermore, the cohesion of its particles is not sufficiently great for it to resist the impression of blows, shocks, &c. If such an article be subjected to the action of heat, its volume first decreases, then it begins to lose water, and shrinks still further. On the other hand, a great coherence of particles is obtained, and thus burnt clay has the hardness of stone. Pure clay, however, shrinks so considerably when burnt that the form given to it is destroyed and cracks easily form; such vessels are also porous, so that they will not hold water. The addition of sand—that is, silica in fine particles—or of chamotte—that is, already burnt and crushed clay—renders the mass much more dense and incapable of cracking in the furnace. Nevertheless, such clay articles (bricks, earthenware vessels, &c.) are still porous to liquids after being burnt, because the clay in the furnace is only baked and does not fuse. In order to obtain articles impervious to water the clay must either be mixed with substances which form a glassy mass in the furnace, permeating the clay and filling up its pores, or else only the surface of the article is covered with such a glassy fusible substance. In the first case the purest kinds of clay give what is known as china, in the second case porcelain or 'faïence,' majolica, &c. Thus, for instance, by covering the surface of clay articles with a layer of the oxides of lead and tin, the well-known white glaze of tiles, &c., is obtained, because the oxides of these metals give a white gloss when fused with silica and clay. In the preparation of china, fluor spar and finely ground silica are mixed up into the clay; these ingredients give a mass which is infusible but softens in the furnace, so that all the particles of the clay cohere in this softened mass, which hardens on cooling. A glaze composed of glassy substances, which only fuse at a high temperature, is also applied to the surface of china articles.

alumina or **aluminium hydroxide**, as a white gelatinous precipitate, which is insoluble in water but easily soluble in acids, even when dilute, and in aqueous soda or potash. The solubility of alumina in acids indicates the basic character of the oxide, and its solubility in alkalis and its power of forming compounds with them show the weakness of this basic character. However, the feeblest acids, even carbonic acid, take up the alkali from such a solution, and the alumina then separates out in a precipitate as the hydroxide. It must also be remembered as characteristic of the salt-forming properties of alumina that it does not combine with such feeble acids as carbonic, sulphurous, or hypochlorous, &c.—that is, its compounds with these acids are decomposed by water. It is also important to observe that the hydroxide is not soluble in aqueous ammonia.

Alumina, Al_2O_3 —that is, the anhydrous aluminium oxide—is met with in nature, sometimes in a somewhat pure state, having crystallised in transparent crystals, which are often coloured by impurities (chromic, cobaltic, and ferric compounds). Such are the ruby and sapphire, the former red and the latter blue. They have a specific gravity 4.0, are distinguished by their very great hardness, which is second only to that of the diamond, and they represent the purest form of alumina. They are found in Ceylon and other islands of the Indian Archipelago, embedded in a rock matrix.^{18a} **Corundum** is the same crystallised anhydrous alumina coloured brown by a trace of oxide of iron. A very much larger portion of this impurity occurs in **emery**, which is found in crystalline masses in Asia Minor and in the State of Massachusetts, and owing to its extreme hardness is employed for polishing stones and metals. In this anhydrous and crystalline state, aluminium oxide is a substance which very powerfully resists the action of reagents, and is insoluble both in solutions of the alkalis

^{18a} Frémy (1890) obtained transparent rubies, which crystallised in rhombohedra, and resembled natural rubies in their hardness, colour, size, and other properties. He heated together a mixture of anhydrous alumina, containing more or less caustic potash, with barium fluoride and bichromate of potassium. The latter is added to give the ruby its colour, and is taken in small quantity (not more than 4 parts by weight to 100 parts of alumina). The mixture was put into a clay crucible, and heated (for from 100 hours to 8 days) in a reverberatory furnace at a temperature approaching 1500°. At the end of the experiment the crucible was found to contain a crystalline mass, and the walls were covered with crystals of the ruby of a beautiful rose colour. It was found that the access of moist air was indispensable for the reaction. According to Frémy, the formation of the ruby may be here explained by the formation of fluoroaluminate of aluminium which under the action of the moist air at the high temperature of the furnace gives the ruby and hydrofluoric acid gas. Alumina easily fuses and sometimes gives crystals like rubies in the heat of the electric furnace or at the temperature produced by the combustion of Al at the expense of Fe_2O_3 (Chap. III., note 42), i.e., about 3000°.

and in strong acids. It is only capable of passing into solution after being fused with alkalis and bisulphate of potassium, KHSO_4 .¹⁹ Alumina may be obtained in this refractory form if the hydroxide be ignited and then fused in the oxyhydrogen flame.²⁰ Alumina also occurs in nature in combination with water—as, for instance, in the rather rare minerals, hydrargillite (sp. gr. 2·3), $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O} = 2\text{Al}(\text{HO})_3$, and diaspora, $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O} = 2\text{AlO}(\text{HO})$ (sp. gr. 3·4). A less pure hydrate, mixed with ferric oxide, sometimes occurs in masses (at Baux in the South of France) and is termed **bauxite**; it contains $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O} = \text{Al}_2\text{O}(\text{HO})_4$ (sp. gr. 2·6). When bauxite is ignited with sodium carbonate, carbonic anhydride is liberated and the alumina then combines with the sodium oxide, forming a saline aluminate of the oxides of aluminium and sodium. This is taken advantage of in practice for the preparation of pure alumina compounds on a large scale, for bauxite is found in large masses (in the South of France, in Austria, and in Carolina in North America), and the resultant compound of alumina and sodium is soluble in water and does not contain ferric oxide. This solution when subjected to the action of carbonic anhydride gives a precipitate of aluminium hydroxide,²¹ which with acids forms aluminium salts. If

¹⁹ The effects of purely mechanical subdivision on the solubility of alumina are evident from the fact that native anhydrous alumina, when converted into an exceedingly fine powder by means of levigation, dissolves in a mixture of strong sulphuric acid and a small quantity of water, especially when heated in a closed tube at 200° , or when fused with acid sulphate of potassium (see Chap. XIII., note 9).

²⁰ When alumina, moistened with a solution of cobalt salt, is ignited, it forms a blue mass called Thénard's salt. This coloration is taken advantage of not only in the arts, but also for distinguishing alumina from other earthy substances resembling it.

²¹ The treatment of bauxite is carried on on a large scale, chiefly in order to obtain alumina from alkaline solutions, free from ferric oxide, because in dyeing it is necessary to have salts of aluminium which do not contain iron. But this end, it would seem, may also be obtained by igniting alumina containing ferric oxide in a stream of chlorine mixed with hydrocarbon vapours, as ferric chloride then volatilises. K. Bayer observed that in the treatment of bauxite with soda, about 4 molecules of sodium hydroxide pass into solution to 1 molecule of alumina, and that on agitating this solution (especially in the presence of some already precipitated aluminium hydroxide), about two-thirds of the alumina is precipitated, so that only 1 molecule of alumina to 12 molecules of sodium hydroxide remains in solution. This solution is evaporated directly, and used again. He therefore treats bauxite directly with a solution of NaHO at 170° in a closed boiler, and on cooling adds hydrated alumina to the resultant solution. The greater part of the dissolved alumina then precipitates on this hydrated alumina, and the solution is used over again. The hydroxide which separates from the alkaline solution has the composition $\text{Al}(\text{OH})_3$. These properties bear a great resemblance to those of boric acid. It is found that the relation between the sodium hydroxide and alumina varies with the mass of water.

If lime is added to a solution of alumina in alkali (sodium aluminate), calcium aluminate is precipitated, from which acids first extract the lime, leaving aluminium hydroxide, which is then easily soluble in acids (Loewig). When sodium aluminate is mixed with a solution of sodium bicarbonate, a double carbonate of the alkali and aluminium is precipitated, which is easily soluble in acids.

aqueous ammonia be added to a solution of aluminium sulphate a gelatinous precipitate is formed, which at first remains suspended in the liquid and then on settling forms a gelatinous mass, which itself indicates the **colloidal property of aluminium hydroxide**. The following points are characteristic of this colloidal state: (1) in an anhydrous state such a colloidal substance is insoluble in water, as alumina is; (2) in the hydrated state, it is gelatinous and insoluble in water; and (3) it is also capable of existing in solutions, from which it separates out in a non-crystalline state, forming a substance resembling glue. These different states of colloids were distinguished by Graham, who gave them the following very characteristic names. He called the gelatinous form of the hydrate **hydrogel**, i.e., a gelatinous hydrate, and the soluble form of the aqueous compound, **hydrosol**, from the Latin for a soluble hydrate. Alumina readily and frequently assumes these states. The gelatinous hydrate of alumina is its hydrogel. Like all similar hydrogels, it shows not the faintest sign of crystallisation; it is apt to vary in many of its properties with the amount of water it contains, and loses its water on ignition, leaving a white powder of the anhydrous oxide. The hydrogel of alumina is soluble both in acids and alkalis. It may also be obtained by the evaporation of its solutions in such feebly energetic acids as volatile acetic acid. These properties are very frequently made use of in the arts, and especially in **the processes of dyeing**, because the hydrogel of alumina in precipitating attracts a number of colouring matters from their solutions, the precipitate being thus coloured by the dyes attracted.²² The preparation of fixed dyes

²² These coloured precipitates of alumina are termed *lakes*, and are employed in dyeing tissues and in the formation of various pigments—such as pastels, oil colours, &c. Thus, if organic colouring matters, such as logwood, madder, &c., are added to a solution of any aluminium salt, and then an alkali added, so that alumina may be precipitated, these pigments, which are by themselves soluble in water, will come down with the precipitate. This shows that alumina is able to combine with the colouring matter, and that this compound is not decomposed by water. The dyes then become insoluble in water. If a dye be mixed with starch paste and aluminium acetate, and then, by means of engraved blocks having a design in relief, we transfer this mixture to a fabric which is then heated, the aluminium acetate will leave the hydrogel of alumina which binds the colouring matter, and water will no longer be able to wash the pigment from the material—that is, a so-called ‘fixed’ dye is obtained. In the case of dyeing a fabric a uniform tint, it is first soaked in a solution of aluminium acetate and then dried, by which means the acetic acid is driven off, while the hydrogel of alumina adheres to the fibres of the material. If the latter be then passed through a solution of a dye in water, the former will be attracted to the portions covered with alumina, and will closely adhere to them. If certain parts of the material be protected by the application of an acid, such as tartaric, $C_4H_6O_6$, oxalic, citric, &c. (these acids being non-volatile), the alumina will be dissolved in those parts, and the pigment will not adhere, so that after washing, a white design will be obtained on those parts which have been so protected.

In dye-works the aluminium acetate is generally obtained in solution by taking a solution of alum, and mixing it with a solution of lead acetate. In this case lead

and the employment of aluminous compounds (mordants) in the processes of dyeing are founded on this fact.²³ When precipitated upon the fibres of tissues (calicoes, linens, &c.) the aluminium hydroxide renders them impermeable to water; this may be taken advantage of for the preparation of waterproof tissues.

The **hydrosol** of alumina—i.e., the soluble aluminium hydroxide—is more difficult to obtain.²⁴ In order to obtain this soluble variety of

sulphate is precipitated and aluminium acetate remains in solution, together with either acetate or sulphate of potassium, according to the amount of acetate of lead first taken. The complete decomposition will be as follows: $\text{KAl}(\text{SO}_4)_2 + 2\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 = \text{KC}_2\text{H}_3\text{O}_2 + \text{Al}(\text{C}_2\text{H}_3\text{O}_2)_3 + 2\text{PbSO}_4$, or the less complete decomposition, $2\text{KAl}(\text{SO}_4)_2 + 3\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 = 2\text{Al}(\text{C}_2\text{H}_3\text{O}_2)_3 + \text{K}_2\text{SO}_4 + 3\text{PbSO}_4$. If the resultant solution of aluminium acetate is evaporated or further boiled, the acetic acid passes off and the hydrogel of alumina remains.

As the salt of potassium obtained in the solution passes away with the water used for washing, and the salt of lead precipitated has no practical use, this method for the preparation of aluminium acetate cannot be considered economical; it is retained in the process of dyeing mainly because both the salts employed, alum and sugar of lead, easily crystallise, and it is easy to judge of their degree of purity in this form. Indeed, it is very important to employ pure reagents in dyeing, because if impurity is present—such as a small quantity of an iron compound—the tint of the dye changes; thus madders give a red colour with alumina, but if oxide of iron is present the red changes into a violet tint. The aluminium hydroxide is soluble in alkalis, whilst ferric oxide is not. Therefore **sodium aluminate**—that is, the dissolved compound of alumina and caustic soda—obtained, as already described, from bauxite, is sometimes employed in dyeing. Every aluminium salt gives a solution containing sodium aluminate free from iron, when it is mixed with excess of caustic soda. This solution, when mixed with a solution of ammonium chloride, gives a precipitate of the hydrogel of alumina: $\text{Al}(\text{OH})_3 + 3\text{NaHO} + 3\text{NH}_4\text{Cl} = \text{Al}(\text{OH})_3 + 3\text{NaCl} + 3\text{NH}_4\text{OH}$. There was originally free soda, and on the addition of sal-ammoniac there is free ammonia, which does not dissolve alumina, so that the hydrogel of the latter is precipitated.

²³ Another direct method for the preparation of pure aluminium compounds consists in the treatment of **cryolite** containing aluminium fluoride, together with sodium fluoride, AlNa_3F_6 . This mineral is exported from Greenland, and is also found in the Urals. It is crushed and heated in reverberatory furnaces with lime, and the resultant mass treated with water; sodium aluminate is then obtained in solution, and calcium fluoride in the precipitate: $\text{AlNa}_3\text{F}_6 + 3\text{CaO} = 3\text{CaF}_2 + \text{AlNa}_3\text{O}_3$.

²⁴ Crum first prepared a solution of basic acetate of alumina—that is, a salt containing as large an excess as possible of aluminium hydroxide with the smallest possible quantity of acetic acid. The solution must be dilute—that is, must not contain more than one part of alumina per 200 of water—and if this solution is heated in a closed vessel (so that the acetic acid cannot evaporate) to the boiling-point of water, for one and a half to two days, the solution, which apparently remains unaltered, loses its original astringent taste, proper to solutions of all the salts of alumina, and has instead the purely acid taste of vinegar. The solution then no longer contains the salt, but acetic acid and the hydrosol of alumina in an uncombined state; they may be isolated from each other by evaporating the acetic acid in shallow vessels at the ordinary temperature. If the solution be diluted with water, it may even be heated to drive off the acetic acid, and with a thin layer of liquid the alumina does not separate as a precipitate. When the acid vapours cease to come off there remains a solution of the hydrosol of alumina, which is tasteless and has no action on litmus paper. When concentrated, this solution acquires a more and more glucy consistency, and when completely evaporated over a water-bath it leaves a non-crystalline glue-like hydrate, the composition of which is $\text{Al}_2\text{H}_4\text{O}_5$.

alumina, Graham took a solution of its hydrogel in hydrochloric acid—that is, a solution of aluminium chloride, which is able to dissolve a still further quantity of the hydrogel of alumina, forming a basic salt having probably the composition, $\text{Al}(\text{HO})\text{Cl}_2$ or $\text{Al}(\text{HO})_2\text{Cl}$. When such a solution, considerably diluted with water, is subjected to dialysis—that is, to diffusion through a membrane²⁵—the hydrochloric acid diffuses through the membrane and leaves the alumina in the form of hydrosol. The resultant solution, even when only containing two or three per cent. of alumina, passes into the hydrogel state with such facility that it is sufficient to transfer it from one vessel to another which has not been previously washed with water, for the entire mass to solidify into a jelly. But a solution containing not more than one-half per cent. of alumina may even be boiled without coagulating; however, after the lapse of several days, this solution will of its own accord yield the hydrogel of alumina.^{25a}

With respect to alumina as a base, it is very important to observe that it is not only capable of combining with other bases,²⁶ but does not give salts with feeble volatile acids (like carbonic and hypochlorous); it forms salts which are easily decomposed by water, especially when heated,²⁷ as well as double and basic

$=\text{Al}_2\text{O}_3, 2\text{H}_2\text{O}$. The smallest quantity of alkalis, and of many acids and salts, will convert the hydrosol into the hydrogel of alumina—that is, convert the aluminium hydroxide from a soluble into an insoluble form, or, as it is said, cause the hydrate to coagulate or gelatinise. Many such colloidal solutions are known (Chap. I., note 57).

²⁵ In a dialyser, Chap. I., note 18.

^{25a} The different states in which the hydrates of alumina occur and are prepared resemble similar varieties of the hydrates of the oxides of iron and chromium, of molybdic and tungstic acids, as well as of phosphoric and silicic acids, of many sulphides, proteid substances, &c. We shall therefore have occasion to recur to this subject in the further course of this work.

The most remarkable peculiarity of Graham's solution is that it solidifies on litmus paper, and leaves a blue ring on it, which shows the alkaline—that is, basic—character of the alumina in such a solution. If in the dialysis the basic hydrochloric acid salt is replaced by a similar acetic acid salt, a hydrosol of alumina is obtained which does not act upon litmus (note 24).

²⁶ Compounds of alumina with bases (aluminates, see note 21) are sometimes met with in nature. Such are spinel, $\text{MgO}, \text{Al}_2\text{O}_3 = \text{MgAl}_2\text{O}_4$; chrysoberyl, BeAl_2O_4 , and others. Magnetic oxide of iron, $\text{FeO}, \text{Fe}_2\text{O}_3 = \text{Fe}_3\text{O}_4$, and compounds like it, belong to the same class. Here we evidently have a case of combination 'by analogy,' as in solutions and alloys, accompanied by the formation of strictly definite saline compounds, and such instances form a clear transition from so-called solutions and certain mixtures to the type of true salts.

²⁷ Not only aluminium acetate (note 24), but also every other aluminium salt with a volatile acid, parts with its acid on heating in aqueous solution—that is, is decomposed by water, and forms either basic salts or a hydrate of alumina. By dissolving aluminium hydroxide in nitric acid we may easily obtain a well-crystallising **aluminium nitrate**, $\text{Al}(\text{NO}_3)_3, 9\text{H}_2\text{O}$, which fuses at 73° without decomposing (Ordway), gives a basic salt, $2\text{Al}_2\text{O}_3, 6\text{HNO}_3$ at 100° , and at 140° leaves the aluminium hydroxide perfectly

salts,²⁸ so that it forms a clear example of a feeble base.²⁹ To these characteristics of alumina we must add that it gives not only compounds of the type AlX_3 , but also of the polymeric type Al_2X_6 , even when X is a simple univalent haloid like chlorine. Deville and Troost showed (1857) that the vapour density of aluminium chloride (at about 400°) is 9.37 with respect to air—that is, nearly 135 with respect to hydrogen, and therefore the formula of its molecule at about 400° is expressed by Al_2Cl_6 , but at higher temperatures (1000° and 1300°) its density corresponds to $AlCl_3$,³⁰ although in the case of boron, arsenic,

free from the elements of nitric acid. But the solutions of this salt, like those of the acetate, are also able to yield aluminium hydroxide. From all this it is evident that we must suppose that the solutions of this and similar salts contain an equilibrated dissociated system, consisting of the salt, the acid, and the base, and their compounds with water, as well as partly the molecules of water itself.

²⁸ As an example of native basic salts we may cite **alunite**, or alum-stone (sp. gr. 2.6), which sometimes occurs in crystals, but more frequently in fibrous masses. It has been found in masses in the Caucasus (at Zaglik, distant forty versts from Elizabetpol), and at Tolfa, near Rome. Its composition is $K_2O, 3Al_2O_3, 4SO_3, 6H_2O$ (alunite contains $9H_2O$). It is soluble in water but is not decomposed by it, but after being slightly ignited it gives up alum to it. It may be artificially prepared by heating a mixture of alum with aluminium sulphate in a closed tube at 230° .

²⁹ As the colloidal properties are particularly sharply developed in those oxides (Al_2O_3 , SiO_2 , MoO_3 , SnO_2 , &c.) which show (like water also) the properties of feeble bases and feeble acids, there is probably some causal reason for this coincidence, all the more so since among organic substances—gelatins, albumins, &c.—the representatives of the colloids also have the property of feebly combining with bases and acids.

³⁰ Since Deville's experiments the question of the density of aluminium chloride has been frequently re-investigated. The subject has more especially occupied the attention of Nilson, Pettersson, Friedel and Crafts, and V. Meyer and his collaborators. In general, it has been found that at low temperatures (up to 440°) the density is constant, and indicates a molecule Al_2Cl_6 ; whilst depolymerisation probably takes place at higher temperatures, and the molecule $AlCl_3$ is obtained. Along with this there has been, and still is, a difference of opinion as to the vapour density of aluminium ethyl and methyl—whether, for instance, $Al(CH_3)_3$ or $Al_2(CH_3)_6$ expresses the molecule of the latter. The interest of these researches is intimately connected with the question of the valency of aluminium, if we hold to the opinion that elements in their various compounds have a constant and strictly definite valency. In this case the formula $AlCl_3$ or $Al(CH_3)_3$ would show that Al is trivalent, and that consequently the compounds of aluminium are $Al(OH)_3$, AlO_3Al , and, in general, AlX_3 . But if the molecule is Al_2Cl_6 , it is—for the followers of the doctrine of the invariable valency of the elements—incompatible with the idea of the trivalency of aluminium, and they assume it to be quadrivalent like carbon, likening Al_2Cl_6 to ethane $C_2H_6 = CH_3CH_3$, although this does not explain why Al does not form $AlCl_4$, or, in general, AlX_4 . In this work another supposition is introduced; according to this, although aluminium, as an element of group III., gives compounds of the type AlX_3 , this does not exclude the possibility of these molecules combining with others, and consequently with *each other*—that is, forming Al_2X_6 ; just as the molecules of univalent elements exist either as H_2 , Cl_2 , &c., or as Na, and the molecules of bivalent elements either as Zn , or as S_2 , or even S_8 . In the first place it must be recognised that the limiting form does not exhaust all power of combination, it only exhausts the capacity of the element for combining with X's; but the saturated substance may afterwards combine with *whole molecules*; a fact best proved by the capacity of substances to form crystalline compounds with water,

and antimony, which give oxides R_2O_3 of the same type as Al_2O_3 , the chlorine compounds always form non-polymeric molecules, BCl_3 , $AsCl_3$, $SbCl_3$.³¹ This duplication (polymerisation) of the form AlX_3 is probably connected with the facility with which the salts of aluminium combine with other salts to form double salts, and with aluminium hydroxide itself to form basic salts.

Aluminium sulphate $Al_2(SO_4)_3$, which is obtained by treating clay or the hydrates of alumina with sulphuric acid, crystallises in the cold with $27H_2O$, or at the ordinary temperature in pearly crystals, which are greasy to the touch and contain $16H_2O$.³² Its solutions act like sulphuric acid—for instance, they evolve hydrogen with zinc, forming

ammonia, &c. But in some substances this faculty for further combinations is less developed (for instance, in carbon tetrachloride, CCl_4), whilst in others it is more so. AlX_3 combines with many other molecules. Now if a limiting form, which does not combine with new X's, nevertheless combines with other whole molecules, it will naturally in some instances combine with itself, will polymerise. In this manner the mind clearly grasps the idea that the same forces which cause S_2 to unite itself to Cl_2 , or C_2H_4 to Cl_2 , &c., also unite molecules of a similar kind together; thus polymerisation ceases to be an isolated fragmentary phenomenon, and chemical combinations 'by analogy' acquire a particular and important interest. In conformity with these views the following proposition may be made concerning the compounds of aluminium. They are of the type AlX_3 in the limit, like BX_3 , but those limiting forms are still able to combine to form $AlX_3.RZ$, and at low temperatures aluminium chloride is a compound of this kind—i.e. $(AlX_3)_2$. In boron, for example, in BCl_3 , this tendency to form further compounds is less developed. Hence boron chloride appears as BCl_3 , and not as $(BCl_3)_2$. Polymerisation is not only possible when a substance has not attained the limit (although it is more probable then), but also when the limiting form has been reached, if only the latter has the faculty of combining with other whole molecules. We may therefore conclude that aluminium, like boron, is trivalent in the same sense that lithium and sodium are univalent, magnesium bivalent, and carbon tetravalent. In a word, there is no reason to consider that aluminium is capable of forming compounds AlX_4 , and in that way to explain the existence of the molecule Al_2Cl_6 . Furthermore, there are many reasons for thinking that AlF_3 , Al_2O_3 , and other empirical formulæ do not express the molecular weights of these compounds, but that they are much higher: Al_nF_{3n} , $Al_{2n}O_{3n}$. Since I introduced this view in the seventies of the past century convincing proofs of the truth of the above statements, and of the independent existence of AlX_3 in a state of vapour have been obtained, for Combes (1889) has determined the vapour density of the volatile aluminium acetylacetonate $Al(C_5H_7O_2)_3$ (which melts at 193° , boils at 315° , and distils without a trace of decomposition), and has found that it exactly corresponds to the above molecular composition. On the other hand, Louise and Roux (1889) by employing the method of 'freezing-point depression' of solutions (Chap. I., note 49) found that the molecules $Al_2(C_2H_5)_6$ and $Al_2(C_5H_{11})_6$, &c., correspond to the type Al_2X_6 . Thus it may now be accepted that the molecular composition of the compounds of aluminium in their simplest form is AlX_3 , but that they may polymerise and give Al_2X_6 or, in general, Al_nX_{3n} .

³¹ In the case of gallium, as a close analogue of aluminium, Lecoq de Boisbaudran (1880) showed that the molecule of gallium chloride probably consists of Ga_2Cl_6 at low temperatures and high pressures, and that it dissociates into $GaCl_3$ at high temperatures and low pressures. The molecule of indium chloride seems to exist only in the simplest form, $InCl_3$.

³² The pure salt ($16H_2O$) is not hygroscopic. In the presence of impurities the amount of water increases to $18H_2O$, and the salt becomes hygroscopic.

basic salts, which are sometimes met with in nature (*aluminite*, $\text{Al}_2\text{O}_3 \cdot 3\text{SO}_3 \cdot 9\text{H}_2\text{O}$, and others)—and may be obtained by the decomposition of normal salts and by the direct solution of the hydroxide in normal salts: these exhibit a varying composition, $(\text{Al}_2\text{O}_3)_n(\text{SO}_3)_m(\text{H}_2\text{O})_q$, where m/n is less than 3. Aluminium sulphate is prepared (pure from the hydrate obtained from bauxite, note 21) in large quantities for dyeing purposes (instead of alums) as a mordant and for the preparation of alums—the ordinary crystalline alum has the composition $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, and ammonium alums (which leave a residue of alumina when ignited) in which the potassium is replaced by ammonium (NH_4). Alums are used in large quantities, because they crystallise so easily. In this respect the alums formed by potassium and ammonium are equally convenient to purify, because they present a considerable difference in their solubility at the ordinary and higher temperatures. If the crystallisation is conducted rapidly, the salt separates in minute crystals, but if slowly deposited, especially in large masses, as in factories, then crystals several centimetres long are sometimes obtained.³³

Aluminium chloride, Al_2Cl_6 , is obtained, like other similar chlorides (for instance MgCl_2), either directly from chlorine and the metal, or by heating to redness an intimate mixture of the amorphous anhydrous oxide and charcoal in a stream of dry chlorine.^{33a} A sublimate is

³³ The sodium alums are very much more soluble, and crystallise with greater difficulty, and are therefore less easily freed from impurities; at 0° , 100 parts of water dissolve 3 parts; at 30° , 22 parts; at 70° , 90 parts; and at 100° , 357 parts of potassium alum. The solubility of ammonium alum is slightly less. The specific gravity of potassium alum is 1.74, that of ammonium alum 1.63, and that of sodium alum 1.60. Alums easily part with their water of crystallisation; thus potash alum partially effloresces when exposed to the air, and loses 9 mol. H_2O under the receiver of an air-pump. At 100° , dry air passed over alums takes up nearly all their water. As we have already mentioned (Chap. XV.), the law of isomorphous substitutions exhibits itself more clearly in the alums than in any other salts, and all alums not only contain the same amount of water of crystallisation, $\text{MR}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ (where $\text{M} = \text{K}, \text{NH}_4, \text{Na}$; $\text{R} = \text{Al}, \text{Fe}, \text{Cr}$), and appear in crystals whose planes are inclined at equal angles, but they also give every possible kind of isomorphous mixture. The aluminium in them is easily replaced by iron, chromium, indium, and sometimes by other metals. while the potassium may be substituted by sodium, rubidium, ammonium, and thallium, and the sulphuric acid may be replaced by selenic and chromic acids. The common form of crystals of alums is octahedral, but if this solution contains a certain small excess of alumina above the ratio $2\text{Al}(\text{OH})_3$ to K_2SO_4 , and not more sulphuric acid than $3\text{H}_2\text{SO}_4$ to $2\text{Al}(\text{OH})_3$, then it easily forms combinations of the cube and octahedron, and these alums are called 'cubic' alums. They are valued by the dyer because they can contain no iron in solution, for oxide of iron is precipitated before alumina, and if the latter be in excess there can be no oxide of iron present. These alums were long exported from Italy, where they were prepared from alunitic (note 28). The potassium alums melt at about 92° , the ammonium alums at 95° , and the sodium alums at about 66° .

^{33a} It is also formed by the action of hydrochloric acid upon metallic aluminium (Nilson and Pettersson), by heating alumina in a mixture of the vapours of naphthalene

obtained because the chloride is very volatile.³⁴ It forms a crystalline readily fusible mass, which deliquesces in the air and dissolves easily in water, with the evolution of a large amount of heat.^{34a} On evaporating this solution, hydrochloric acid and aluminium hydroxide are liberated. But if the solution is heated in a closed tube, with an excess of hydrochloric acid, then, on cooling, crystals of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ are obtained—that is, aluminium chloride both combines with water and is decomposed by it. And the faculty of the type AlX_3 for combining with other molecules is seen in the compounds of AlCl_3 with many other chlorine compounds. Thus, for example, a mixture of aluminium chloride with sulphur tetrachloride gives $\text{Al}_2\text{Cl}_6 \cdot \text{SCl}_4$, under the action of chlorine, whilst with phosphorus pentachloride it forms $\text{AlCl}_3 \cdot \text{PCl}_5$. The compounds $\text{AlCl}_3 \cdot \text{NOCl}$, $\text{AlCl}_3 \cdot \text{POCl}_3$, $\text{AlCl}_3 \cdot 3\text{NH}_3$, $\text{AlCl}_3 \cdot \text{KCl}$, $\text{AlCl}_3 \cdot \text{NaCl}$ are also known.³⁵ The compound of aluminium and sodium chlorides,

and HCl (Faure, 1889), and by the action of dry HCl upon an alloy of 14 per cent. or more of Al with copper (Mobery).

³⁴ Aluminium chloride fuses at 178° , boils at 183° (pressure 755 mm., at 168° under a pressure of 250 mm., and at 213° under 2,278 mm.), according to Friedel and Crafts, so that it boils immediately after fusion. According to Seubert and Pallard (1892) Al_2Cl_6 fuses at 193° . Aluminium bromide fuses at about 92° , and the iodide at 185° according to Weber and at 125° according to Deville and Troost.

All these halogen compounds of aluminium are soluble in water. **Aluminium fluoride**, AlF_3 (Al_nF_{3n}), is insoluble in water; however, a solution is formed by dissolving alumina in hydrofluoric acid with an excess of acid. This solution probably contains the hydrosol of alumina or a compound of AlF and HF . When the solution is evaporated crystals of $\text{Al}_2\text{F}_6 \cdot \text{HF} \cdot \text{H}_2\text{O}$ are obtained which are insoluble in water. If this solution is saturated with a still larger amount of alumina, it deposits crystals having the composition, $\text{Al}_2\text{F}_6 \cdot 7\text{H}_2\text{O}$, when evaporated. Perhaps the soluble form consists of AlF_3 and the insoluble one of a polymeride, Al_2F_6 . All these compounds, when ignited, leave insoluble anhydrous aluminium fluoride. It forms colourless rhombohedra, which are non-volatile, of sp. gr. 3.1, and are decomposed by steam into alumina and hydrofluoric acid. The acid solution apparently contains a compound which has its corresponding salts; by the addition of a solution of potassium fluoride, a gelatinous precipitate of AlK_3F_6 is obtained. A similar compound occurs in nature—namely, AlNa_3F_6 , or **cryolite**, sp. gr. 3.0.

^{34a} In this respect aluminium chloride resembles the chlor-anhydrides of the acids, and probably in the aqueous solution the elements of the hydrochloric acid are already separated, at least partially, from the aluminium hydroxide. The solution may also be obtained by the action of aluminium hydroxide on hydrochloric acid.

³⁵ Here we see an example in confirmation of what has been said in note 30—i.e., the action of the molecule AlCl_3 . We shall cite still another instance confirming the power of alumina to enter into complex combinations. Alumina, moistened with a solution of calcium chloride, gives, when ignited, an anhydrous crystalline substance (tetrahedral), which is soluble in acids, and has the composition $(\text{Al}_2\text{O}_3)_6(\text{CaO})_{10}\text{CaCl}_2$. Even clay forms a similar stony substance which might be of practical use.

Among the most complex compounds of aluminium, **ultramarine**, or **lapis lazuli**, must be mentioned. It occurs in nature near Lake Baikal, in crystals, some colourless and others of various tints—green, blue, and violet. When heated it becomes dull and acquires a very brilliant blue colour. In this form it is used for ornaments (like malachite), and as a brilliant blue pigment. At the present time ultramarine is prepared artificially in large quantities as a paint, and this process is one of the most important

AlNaCl_4 , is very fusible and much more stable in the air than aluminium chloride itself. It seems to be of the same type as the alums. This compound, AlNaCl_4 , was for a long time employed in the extraction of metallic aluminium, as we shall presently proceed to describe. Aluminium bromide, which is obtained by the direct combination of metallic aluminium with bromine, closely resembles the chloride; it melts at 90° , volatilises at 270° . Aluminium iodide is obtained by heating iodine with finely divided aluminium in a closed tube; it is so easily decomposed by oxygen that its vapour even explodes when mixed with it.³⁶

Metallic aluminium was first prepared by Wöhler in 1822 as a grey powder by the action of potassium on aluminium chloride. He afterwards (in 1845) obtained it as a white compact metal, unoxidisable in the air, and only slowly attacked by acids. Owing to the abundant and widespread occurrence of compounds of aluminium, many efforts have been made in investigating in detail the methods for the extraction of this metal. These efforts were brought to a successful issue (1845) by Sainte-Claire Deville, who is also renowned for his doctrine of dissociation. Experiments on a large scale have proved that metallic aluminium, although possessed of great lightness, strength, and durability, is not so generally suitable for technical purposes as was at first thought. Nitric and many other acids (especially organic), indeed, do not act on it, but the alkalis, dilute solutions of NH_3 and its salts, and even

conquests of science; for the blue tint of ultramarine has been the object of many scientific researches, which have culminated in the manufacture of this natural substance. The most characteristic property of ultramarine is that when placed in sulphuric acid it evolves hydrogen sulphide and becomes colourless. This shows that the blue colour of ultramarine is due to the presence of sulphides. If clay be heated in a furnace with sodium sulphate and charcoal (forming sodium sulphide) without access of air, a white mass is obtained, which becomes green when heated in the air, and when treated with water leaves a colourless substance known as 'white ultramarine.' When ignited in the air it absorbs oxygen and turns blue. The coloration is ascribed to the presence of metallic sulphides or polysulphides; but it is most probable that silicon sulphide, or its oxysulphide, SiOS , is present. At all events the sulphides play an important part, but the problem is not yet quite settled. The formula $\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}\text{S}$ is ascribed to white ultramarine. The green probably contains more sulphur, and the blue a still larger quantity. The last is supposed to have the composition $\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}\text{S}_3$. It is more probable (according to Guckelberger, 1882) that the composition of the blue form varies between $\text{Si}_{18}\text{Al}_{18}\text{Na}_{20}\text{S}_6\text{O}_{71}$ and $\text{Si}_{18}\text{Al}_{12}\text{Na}_{20}\text{S}_6\text{O}_{69}$. The latter may be expressed as $(\text{Al}_2\text{O}_3)_6(\text{SiO}_2)_{18}(\text{Na}_2\text{O})_{10}\text{S}_6\text{O}_5$, which would indicate the presence of insufficiently oxidised sulphur in ultramarine.

³⁶ At the ordinary temperature aluminium does not decompose water, but if a small quantity of iodine, or of hydriodic acid and iodine, or of aluminium iodide and iodine, is added to the water, then hydrogen is abundantly evolved. It is evident that here the reaction proceeds owing to the temporary formation of AlI_3 , and that this substance, with water, gives aluminium hydroxide and hydriodic acid, which, with aluminium, evolves hydrogen and re-forms AlI_3 . Aluminium probably belongs to those metals having a greater affinity for oxygen than for the halogens (note 36b).

moist table salt, humidity, &c.,^{36a} tarnish it, and hence objects made of aluminium suffer at the surfaces and alter, and the metal cannot, as was hoped, replace the precious metals, from which it differs in its extreme lightness. But the alloys made with aluminium (especially with copper, for example, aluminium bronze) are very valuable in their properties and applications.

Neither charcoal nor zinc will reduce the oxygen compounds of aluminium; even sodium and potassium do not act on alumina. Moreover, metallic aluminium, like magnesium, is able to reduce even the metals of the alkalis from their oxygen compounds. This is connected with the fact that the atom of oxygen evolves more heat in combining with Al (and Mg) than it does in combining with other metals; whilst, on the other hand, chlorine (and the other halogens) evolves more heat in combining with the metals of the alkalis.^{36b}

The Deville method for the preparation of metallic aluminium is based on the decomposition of the above-mentioned compound of sodium and

^{36a} As an example we may mention that if mercury comes into contact with metallic aluminium, and especially if it is rubbed upon the surface of aluminium moistened with a dilute acid, the Al becomes rapidly oxidised (Al_2O_3 being formed). The oxidation is accompanied by a very curious appearance, as it were, of wood (or fur) formed by threads of oxide of aluminium growing upon the metal. This was first pointed out by Cass in 1870, and subsequently by A. Sokoleff in 1892. This interesting and curious phenomenon leads to the formation of alumina. It does not proceed in an atmosphere of nitrogen, but takes place in a few minutes in ordinary air.

I think it necessary, however, to add that according to Lubbert and Rascher's researches (1891), wine, coffee, milk, oil, urine, earth, &c., have no more action upon aluminium vessels than upon copper, tin, and other similar articles. In the course of four months ordinary vinegar dissolved 0.35 grm. of Al per sq. centimetre, whilst a 5 per cent. solution of common salt dissolved about 0.05 grm. of aluminium. Ditte (1890) showed that Al is acted upon by nitric and sulphuric acids, although only slowly (owing to the formation of a layer of gas, as in Chap. XVI., note 10), and that the reaction proceeds much more rapidly *in vacuo* or in the presence of oxidising agents. Al is even oxidised by water on the surface, but the thin coating of alumina formed prevents further action. In the course of twelve hours nitric acid of sp. gr. 1.383 dissolved at 17° about 20 grms. of aluminium (containing only a small amount of Si, 1— $\frac{1}{4}$ per cent.) from a sq. metre of surface (Le Rouart, 1891). A solution of NaCl produces oxidation: $\text{Al}_2 + 6\text{NaCl} + 3\text{H}_2\text{O} = \text{Al}_2\text{Cl}_6 + 3\text{Na}_2\text{O} + 3\text{H}_2$, and then: $\text{Al}_2\text{Cl}_6 + 3\text{Na}_2\text{O} = \text{Al}_2\text{O}_3 + 6\text{NaCl}$, so that the salt is renewed. Güttig (1896) showed that the action of a dilute solution of NH_3 on Al leads to the formation of an ammoniacal compound of the hydrate of alumina with the evolution of hydrogen, and that the presence of ammoniacal salts facilitates the action.

^{36b} In addition to the data given in Chaps. XI., XIII., and in Chap. XV., note 19, the following are the amounts of heat in thousands of units evolved in the formation of the oxides and chlorides from the metals taken in gram-atomic quantities:

Na_2O 100; MgO 140*; $\frac{1}{2} \text{Al}_2\text{O}_3$ 120*; $\frac{1}{2} \text{Fe}_2\text{O}_3$ 63*;
 Na_2Cl_2 195; MgCl_2 151; $\frac{1}{2} \text{Al}_2\text{Cl}_6$ 107; $\frac{1}{2} \text{Fe}_2\text{Cl}_6$ 64.

The asterisks following the oxides of Mg, Al, and Fe call attention to the fact that the existing data refer to the formation of the hydrates of these metals, from which the heats of formation of the anhydrous oxides are only assumed, because the heats of hydration (for example, $\text{MgO} + \text{H}_2\text{O}$) have not yet been determined.

aluminium chlorides by metallic sodium. The compound is obtained by passing the vapour of aluminium chloride (evolved from a mixture of alumina, extracted from bauxite or cryolite, with charcoal ignited in a stream of chlorine) over red-hot salt, when the compound AlNaCl_4 is itself volatilised, and may in this manner be obtained pure. A mixture of this compound with salt and fluor spar, or with cryolite, is heated with a certain excess of sodium, cut into small lumps. On a large scale this operation is carried on in special furnaces with a small access of air and at a high temperature: $\text{NaAlCl}_4 + 3\text{Na} = 4\text{NaCl} + \text{Al}$. Deville's method, which in the sixties of the nineteenth century gave the first large quantities of aluminium and the possibility of testing its applications in the arts, was complicated and expensive, and did not

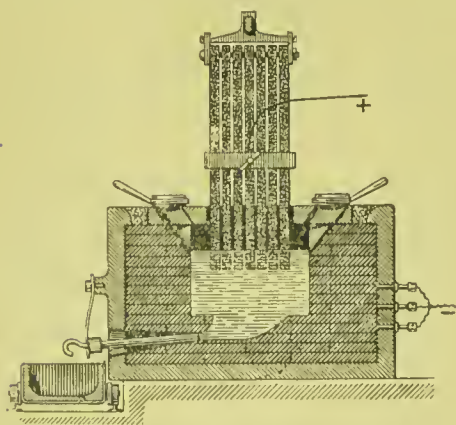


FIG. 92.—Héroult's electric furnace for preparing alloys of aluminium.

give metal sufficiently pure for many purposes, for instance, for replacing copper in electric conductors. Therefore when the dynamo was perfected in the eighties, many processes (Héroult, 1887, Borchers, Grabau, &c.) appeared for the preparation of aluminium by electrolysis at the high temperatures of the electric furnace. Bunsen (1854) and Deville (1854) had already obtained aluminium by electrolysis.

Since the close of the eighties the metallurgy of aluminium has

taken a new direction, based upon the action of an electric current upon cryolite at a high temperature,³⁷ and the solution of oxide of aluminium (obtained from bauxite or in the form of corundum) in it; under these conditions metallic aluminium is reduced at the negative pole (cathode) in a sufficiently pure state, and, if the cathode be copper, forms alloys with it. Such are Hall's and Cowles's (both in the United States) and the Neuhausen process (where the current is obtained from a dynamo worked by the Falls of the Rhine at Schaffhausen). As an example, we shall describe (in the words of Prof. D. P. Konovallöf, who became acquainted with this process at the Chicago Exhibition) Hall's process as applied near Pittsburg, where it gives about 1,500 kilos of Al a day.

³⁷ Cryolite under the action of the current at about 1000° gives off the vapour of Na which reduces the Al, but it recombines with the liberated fluorine and again passes into the fused mass, which is able to dissolve alumina and so give a further quantity of Al. The alumina is either added from time to time or absorbed from the lining of the furnace.

An iron box (about 1 metre long and $\frac{1}{2}$ metre wide), provided with a well-rammed-down charcoal lining, is charged with a mixture of cryolite and Al_2O_3 (from bauxite), over which salt is strewn, and a current of 5,000 ampères at 20 volts is passed through the mixture. The anode is composed of a carbon cylinder (about 9 cm. in diameter), while the charcoal lining forms the cathode. When the temperature inside the box is raised to a red heat by the current, the mixture fuses and the Al_2O_3 begins to decompose. The Al liberated collects at the bottom of the box, whilst the oxygen evolved burns the charcoal anode. When the decomposition is at an end, and the resistance of the mass increases, a fresh quantity of Al_2O_3 is added, and this is continued until the amount of impurities accumulated in the furnace and passing into the metal becomes too great.^{37a}

Aluminium has a white colour slightly resembling that of tin—that is, it is greyer than silver and has the slightly dull lustre of tin, but, compared with tin and pure silver, aluminium is very hard. Its density is 2.67—that is, it is nearly four times as light as silver and three times as light as copper. It melts at an incipient red heat (600°), and in so doing is but slightly oxidised. At the ordinary temperature it does not alter in the air, and in a compact mass it burns with great difficulty at a white heat, but in thin sheets, into which it may be rolled, or as a very fine wire, it burns with a brilliant white light, since it forms an infusible and non-volatile oxide with the evolution of about 350,000 units of heat for Al_2O_3 (102 grms.). Aluminium itself is non-volatile at a furnace heat. These properties render it a very good reducing agent, and N. N. Beketoff showed that it reduces the oxides of the alkali metals (Chap. XIII., note 42a). Aluminium reduces iron, chromium, and similar metals from their oxides with still greater facility, and the reaction, owing to the comparatively small specific heat (and small amount) of the resulting substances, is accompanied by a powerful rise of temperature, sufficient not only to fuse the iron and oxide of aluminium,

^{37a} The cost of working this process can be brought as low as tenpence per lb., or about two shillings per kilo. In England, Castner, prior to the introduction of the electric method, obtained Al by taking a mixture of 1,200 parts of the double salt NaAlCl_4 , 600 parts of cryolite, and 350 parts of Na, and obtained about 120 parts of Al, so that the cost of this process is about $1\frac{1}{2}$ time that of the electric method.

Buchner found that sulphide of aluminium, Al_2S_3 , is more suitable for the preparation of Al by the electrolytic method than Al_2O_3 , but since the formation of Al_2S_3 by heating a mixture of Al_2O_3 and charcoal in sulphur vapour proceeds with difficulty, Gray (1894) proposed to prepare Al_2S_3 by heating a mixture of charcoal, sulphate of aluminium, and sodium fluoride. The resultant molten mixture of NaF and Al_2S_3 gives aluminium directly under the action of an electric current. The production of 1 kilo of aluminium consumes about 30–50 h.p. per hour at the present day. At its present price—three francs per kilo—aluminium can compete with copper in equal volumes.

but also to yield very high temperatures. Thus 'thermite' (Goldsmith) or a mixture of aluminium powder and powdered oxide of iron (see Chap. III., note 42) is used for obtaining high (up to 3000°) temperatures and for welding iron. The reaction proceeds according to the equation: $\text{Fe}_2\text{O}_3 + 2\text{Al} = \text{Al}_2\text{O}_3 + 2\text{Fe}$, and corresponds to the evolution of about 150,000 units of heat per 54 parts of aluminium.^{37b} The comparative lightness of aluminium and the great ease with which it takes up oxygen from even the metals of the alkalis are in apparent contradiction to the fact of its being unoxidised by exposure to the air. This is apparently due to a thin, transparent layer of oxide (Ditte) being formed as a coating over the metal, because the metal in the form of powder (the surface is then greater) always contains much oxide. If a solution of corrosive sublimate is poured over metallic aluminium (or even if the metal is simply moistened with the solution) the mercury is reduced and forms an amalgam in which the aluminium becomes oxidised with great ease and decomposes water at the ordinary temperature. This action is probably assisted by the fact that a galvanic couple (mercury-aluminium) is formed, and also by the formation of a renewed bright fresh surface of aluminium (see note 36a). Amalgamated aluminium is prepared (according to Wislicenus, 1895) by pouring a 0.5 per cent. solution of HgCl_2 over aluminium powder or shavings previously washed with an alkali, and quickly washing with water, alcohol, ether, and benzene directly hydrogen begins to be given off. The amalgam should be kept under benzene. As it decomposes water with the evolution of hydrogen it may be used as an excellent neutral reducing agent—for instance, for reducing the oxides of nitrogen and nitro-compounds, and also for removing water from alcohol, &c. Dilute sulphuric acid has scarcely any action on Al, but the strong acid dissolves it. Nitric acid also does not dissolve it. On the other hand, hydrochloric acid, caustic potash, and ammonia dissolve aluminium. In the latter cases hydrogen is evolved.³⁸

^{37b} A mixture of the oxides of Fe, Cr, &c., with aluminium powder may be ignited, according to Goldsmith, by means of special capsules containing a mixture of peroxide of barium and aluminium powder. The capsules burn very violently and rapidly. But 'thermite' may also be ignited directly by means of a magnesium wire set into its midst.

³⁸ Aluminium, when heated to the high temperature of the electric furnaces, dissolves carbon and forms an alloy which, according to Moissan, when rapidly treated with cold hydrochloric acid, leaves a compound C_3Al_4 in the form of a yellow crystalline transparent substance of sp. gr. 2.36. This carbide of aluminium, C_3Al_4 , corresponds to methane, CH_4 , for Al replaces H_3 and carbon O_2 or H_4 , that is, it is equal to three molecules of CH_4 with the substitution of twelve atoms of H in it by four of Al, or, what is the same thing, it is the duplicated molecule of Al_2O_3 with the substitution of O_6 by C_3 . And indeed C_3Al_4 under the action of water forms marsh gas and hydrate of alumina: $\text{C}_3\text{Al}_4 + 12\text{H}_2\text{O} = 3\text{CH}_4 + 4\text{Al}(\text{OH})_3$. This decomposition presents a new aspect of the syn-

Aluminium forms alloys with different metals with great ease. Among them the copper alloy is the only one of practical use. It is called **aluminium bronze**. This alloy is prepared by dissolving 11 per cent. by weight of metallic aluminium in molten copper at a white heat. The formation of the alloy is accompanied by the development of a considerable quantity of heat, so that it glows to a bright white heat. This alloy (Chap. XV., note 19b), which corresponds with the formula AlCu_3 , presents an exceedingly homogeneous mass, especially if perfectly pure copper is taken. It is distinguished for its capacity to fill up the most minute impressions of the mould into which it may be cast, and by its extraordinary elasticity and toughness, so that objects cast from it may be hammered, drawn, polished, &c. A wire made of this alloy, 1 sq. mm. in section, breaks under a load of 60 kilos (almost the same as for steel and greater than with iron and copper) with an elongation of 24 per cent. Its specific gravity is 7.7. Its surface remains almost unchangeable in the air, and it has a colour and lustre which may be compared to that of gold alloys. Hence aluminium bronze is much used in the arts for making spoons, watches, vessels, forks, knives, and for ornaments, &c. No less important is the fact that the admixture of the one-thousandth part of aluminium with steel renders its castings homogeneous (free from cavities) to an extent that could not be arrived at by other means; nor does the quality of the steel deteriorate in any respect by this admixture, but rather is it improved. In a pure state, aluminium is only employed for such objects as require the hardness of metals with comparative lightness, such as telescopes and various physical apparatus and small articles, &c. Among the alloys of aluminium, **magnalium**, containing from 10 to 25 per cent. of magnesium, deserves to be mentioned, as it is lighter than aluminium, having the sp. gr. about 2.2. It is unchangeable in the air, is easily cast, hard and tough, and takes so fine a polish that it can be used for making mirrors (when it contains about 20 per cent. Mg).

According to the periodic system of the elements, the analogues of magnesium are zinc, cadmium, and mercury in the second group. So also in the third group, to which aluminium belongs, we find its corresponding analogues **gallium**, **indium**, and **thallium**. They are all three so rarely and sparingly met with in nature that they could only be discovered by means of the spectroscope. This fact shows that they

thesis of hydrocarbons, and quite agrees with what should follow from the action of water upon the metallic carbides as applied by me for explaining the origin of naphtha (Chap. VIII., notes 57, 58, and 69). Frank (1894) by heating Al with carbon obtained a similar although not quite pure compound, which (like CaC_2) evolves acetylene with hydrochloric acid, and hence probably has the composition AlC_3 .

are partially volatile, as should be the case according to the properties of their nearest neighbours, the very volatile zinc, cadmium, and mercury. As with them, in gallium, indium, and thallium the density of the metal, decomposability of compounds, &c., rise with the atomic weight. But here we find a peculiarity which does not exist in the second group. With magnesium, zinc, cadmium, and mercury, the fusibility increases with the atomic weight; indeed, the heaviest metal—mercury—is a liquid. In the third group it is not so. In order to understand this it is sufficient to turn our attention to the elements of the further groups of the uneven series—for instance, to group V., containing phosphorus, arsenic, and antimony, or to group VI., with sulphur, selenium, and tellurium, and also to group VII., where chlorine, bromine, and iodine are situated. In all these instances the fusibility decreases with a rise of atomic weight; the members of the higher series, the elements of a high atomic weight, fuse with greater difficulty than the lighter elements. The elements of the uneven series of group III., aluminium, gallium, indium, thallium, forming, as they do, a transition, all show an intermediate behaviour. Here the most fusible of all is the medium metal gallium,^{38a} which fuses at the heat of the hand; whilst indium, thallium, and aluminium fuse at much higher temperatures.

Zinc (group II.), which has an atomic weight 65, should be followed in group III. by an element with an atomic weight of about 69. It will be in the same group as Al, and should consequently give R_2O_3 , RCl_3 , $R_2(SO_4)_3$, alums, and similar compounds analogous to those of aluminium. Its oxide should be more easily reducible to metal than alumina, just as zinc oxide is more easily reduced than magnesia. The oxide R_2O_3 should, like alumina, have feeble but clearly expressed basic properties. The metal reduced from its compounds should have a greater atomic volume than zinc, because in the fifth series, proceeding from zinc to bromine, the volume increases. And as the volume of zinc is 9.2, and that of arsenic 18, our metal should have a value near to 12. This is also evident from the fact that the volume of aluminium is 11, and that of indium 14, and our metal is situated in group III., between aluminium and indium. If its volume is 11.5, and its atomic weight about 69, then its density will be nearly 5.9. The fact that zinc is more volatile than magnesium gives reason for thinking that the metal in question will be more volatile than

^{38a} The same is the case in group IV. of the uneven series, where tin is the most fusible. Thus the temperature of fusion rises on both sides of tin (silicon is very infusible; germanium, 900°; tin, 230°; lead, 326°); as it also does in group III., starting from gallium, for indium fuses at 176°, less easily than gallium but more easily than thallium (294°). Aluminium also fuses with greater difficulty than gallium.

aluminium, and therefore for expecting its discovery by the aid of the spectroscope, &c.

These properties were indicated by me for the analogue of aluminium in 1871, and I named it (see Chap. XV.) **eka-aluminium**. In 1875 Lecoq de Boisbaudran, who had done much work in spectrum analysis, discovered a new metal in a zinc blende from the Pyrenees (Pierrefitte). He recognised its individuality and difference from zinc, cadmium, indium, and the other companions of zinc by means of the spectroscope; but he only obtained some fractions of a centigram of it in a free state. Consequently only a few of its reactions were determined, as, for instance, that barium carbonate precipitates the new oxide from its salts (alumina, as is known, is also precipitated). Lecoq de Boisbaudran named the newly discovered metal **gallium**. As one would expect the same properties for eka-aluminium as were observed in gallium, I pointed out this fact at the time in the 'Memoirs' of the Paris Academy of Sciences. All the subsequent observations of Lecoq de Boisbaudran confirmed the identity between the properties of gallium and those indicated for eka-aluminium. Immediately after this the ammonium alum of gallium was obtained, but the most convincing proof of all was found in the fact that the density of gallium, although first apparently different (4.7) from that indicated above, afterwards, when the metal was carefully purified from sodium (which was first used as a reducing agent), proved to be just that (5.9) which would have been looked for in the analogue of aluminium; and, what was very important, the equivalent (23.3) and atomic weight (69.8) determined by the specific heat (0.08) were shown by experiment to be such as would be expected. These facts confirmed the universality and applicability of the periodic system of the elements. It must be remarked that previous to it there was no means of foretelling either the properties or even the existence of undiscovered elements.³⁹

Much more light has been thrown on the following element of the

³⁹ The spectrum of gallium is characterised by a brilliant violet line of wave-length = 417 millionths of a millimetre. The metal can be separated from the solution, containing a mixture of the many metals occurring in the zinc blende, by making use of the following reactions: it is precipitated by sodium carbonate in the first portions; it gives a sulphate which, on boiling, easily changes into a basic salt, very slightly soluble in water; and it is deposited in a metallic state from its solutions by the action of a galvanic current. It fuses at $+30^{\circ}$, and, when once fused, remains liquid for some time. It oxidises with difficulty, evolves hydrogen from hydrochloric acid and from potassium hydroxide, and, like all feeble bases (for instance, alumina and indium oxide), it readily forms basic salts. The hydroxide is soluble in a solution of caustic potash, and slightly so in caustic ammonia. Gallium forms volatile GaCl_3 and GaCl_2 (Nilson and Pettersson).

aluminium group, **indium**, In, which occurs in small quantities in certain zinc ores. It was discovered (1863) by Reich and Richter (and more fully investigated by Winkler) in the Freiberg zinc ores, and was named indium from the fact that it gives to the flame of a gas-burner a blue coloration, owing to the indigo blue spectral lines proper to it (wavelength 451 millionths of 1 mm.). The equivalent (see Chap. XV., note 15), specific heat, and other properties of the metal confirm the atomic weight $\text{In} = 114$ and the composition of its oxide In_2O_3 .⁴⁰

Inasmuch as we found among the analogues of magnesium in group II. a metal, mercury, heavier and more easily reduced than the rest, and giving two degrees of oxidation, so we should expect to find among the analogues of aluminium in group III. a metal which would be heavy, easily reduced, and give two grades of oxidation, and would have an atomic weight greater than 200. Such is **thallium**. It forms compounds of a lower type, TlX , besides the higher unstable type TlX_3 , just as mercury gives HgX_2 and HgX . In the form of thallic oxide, Tl_2O_3 , it gives a feebly energetic base, as would be expected by analogy with the oxides Al_2O_3 , Ga_2O_3 , and In_2O_3 , whilst in thalrous oxide, Tl_2O , the basic properties are sharply defined, as might be expected according to the properties of the type R_2O (Chap. XV.). **Thallium** was discovered in 1861 by Crookes and by Lamy in certain pyrites. When pyrites are employed in the manufacture of sulphuric acid, they are burned, and give, besides sulphurous anhydride, the vapours of various substances which accompany the sulphur and are volatile. Among these substances arsenic and selenium are found, and, together with them, thallium. These substances accumulate in a more or less considerable quantity in the tubes through which the vapours formed in the combustion of the pyrites have to pass. When the methods of spectrum analysis were discovered (1860), a great number of substances were subjected to

⁴⁰ The vapour density of indium chloride, InCl_3 (note 31), determined by Nilson and Pettersson, confirms this atomic weight. Indium is separated from zinc and cadmium, with which it occurs, by taking advantage of the facts that its hydroxide is insoluble in ammonia, that the solutions of its salts give indium when treated with zinc (hence indium is dissolved after zinc by acids) and that they give a precipitate with hydrogen sulphide even in acid solutions. Metallic indium is grey, has a sp. gr. of 7.42, fuses at 176° , and does not oxidise in the air; when ignited it first gives a black suboxide, In_4O_3 , then volatilises and gives a brown oxide, In_2O_3 , whose salts, InX_3 , are also formed by the direct action of acids on the metal, hydrogen being evolved. Caustic alkalis do not act on indium, from which it is evident that it is less capable of forming alkaline compounds than aluminium is; however, with potassium and sodium hydroxides, solutions of indium salts give a colourless precipitate of the hydroxide, which is soluble in an excess of the alkali, like the hydroxides of aluminium and zinc. Its salts do not crystallise. Nilson and Pettersson (1889), by the action of HCl upon In, obtained volatile, crystalline, InCl_2 , and by treating this compound with In, InCl also.

spectroscopic research, and it was observed that those sublimations which are obtained in the combustion of certain pyrites contained an element having a very sharply defined and characteristic spectrum—namely, in the green portion of the **spectra** it gave a well-defined **green band** (wave-length 535 millionths millimetre) which did not correspond with any then known element.⁴¹

Under the action of a galvanic current solutions of thallium salts deposit the metal in the form of a heavy powder. It is of a grey colour like tin, is soft like sodium, and has a metallic lustre. Its specific gravity is 11.8, it melts at 290°, and volatilises at a high temperature. When heated slightly above its melting-point it forms an insoluble (in water) higher oxide, Tl_2O_3 , as a dark-coloured powder, generally, however, accompanied by the lower oxide Tl_2O , which is also black, but soluble in water and alcohol. This solution has a distinctly

⁴¹ Thallium was afterwards found in certain micas and in the rare mineral crookesite, containing lead, silver, thallium, and selenium. Its isolation depends on the fact that in the presence of acids thallium forms thallous compounds, TlX . Among these compounds the chloride and sulphate are only slightly soluble, and give with hydrogen sulphide a black precipitate of the sulphide, Tl_2S , which is soluble in an excess of acid, but insoluble in ammonium sulphide. The best method of preparing thallous hydroxide, $TlOH$, is by the decomposition of the requisite quantity of baryta by thallous sulphate, which is slightly soluble in water; barium sulphate is then obtained in the precipitate and thallous hydroxide in solution. This solubility of the hydroxide is exceedingly characteristic, and forms one of the most important properties of thallium. These lower (thallous) compounds are of the type TlX , and recall the salts of the alkalis. The salts TlX are colourless, do not give a precipitate with the alkalies or ammonia, but are precipitated by ammonium carbonate, because thallous carbonate, Tl_2CO_3 , is sparingly soluble in water. Platinic chloride gives the same kind of precipitate as it does with salts of potassium—that is, thallous platinichloride, $PtTl_2Cl_6$. All these facts, together with the isomorphism of the salts TlX with those of potassium, again point out what an important significance the types of compounds have in the determination of the character of a given series of substances. Although thallium has a greater atomic weight and greater density than potassium, and although it has less atomic volume, nevertheless thallous oxide is analogous to potassium oxide in many respects, for they both give compounds of the same type, RX . We may further remark that thallous fluoride, TlF , is readily soluble in water, as also is thallous silicofluoride, $SiTl_2F_6$, but that thallous cyanide, $TlCN$, is sparingly soluble in water. This, together with the slight solubility of thallous chloride, $TlCl$, and sulphate, Tl_2SO_4 , indicates an analogy between TlX and the salts of silver, AgX .

As regards the higher oxide or the **thallic oxide**, Tl_2O_3 , the thallium is trivalent in it—that is, it forms compounds of the type TlX_3 . The hydroxide, $TlO(OH)$, is formed by the action of hydrogen peroxide on thallous oxide, or by the action of ammonia on a solution of thallic chloride, $TlCl_3$. It is obtained as a brown precipitate, insoluble in water but easily soluble in acids, with which it gives thallic salts, TlX_3 . **Thallic chloride**, $TlCl_3$, which is obtained by cautiously heating the metal in a stream of chlorine, forms an easily fusible white mass, which is soluble in water and able to part with two-thirds of its chlorine when heated. An aqueous solution of this salt yields colourless crystals containing one equivalent of water. It is evident from the above that all the thallic salts can be easily reduced to thallous salts by reducing agents such as sulphurous anhydride, zinc, &c. Besides these salts, thallic sulphate, $Tl_2(SO_4)_3 \cdot 7H_2O$, thallic nitrate, $Tl(NO_3)_3 \cdot 4H_2O$, &c., are known. These salts are decomposed by water, like the salts of many feebly basic metals—for example, aluminium.

alkaline reaction. This **thallous oxide** melts at 300° , and is easily obtained from the hydroxide, $TlHO$, by igniting it without access of air (in the presence of air the incandescent thallous oxide passes partly into thallic oxide). **Thallous hydroxide**, $TlOH$, crystallises with one molecule of H_2O in yellow prisms which are very easily soluble in water. Metallic thallium may be used for its preparation, as the metal in the presence of water attracts oxygen from the air and forms the hydroxide. But metallic thallium does not decompose water, although it gives a hydroxide which is soluble in water. All the other data for the chemical and physical properties of thallium, of its two degrees of oxidation and of their corresponding salts, are expressed by the position occupied by this metal in virtue of its atomic weight $Tl = 204$, between mercury $Hg = 200$, and lead $Pb = 207$.

Gallium, indium, and thallium belong to the uneven series, and there should be elements of the even series in group III. corresponding with calcium, strontium, and barium in group II. These elements should in their oxides, R_2O_3 , present basic characters of a more energetic nature than those shown by alumina, just as calcium, strontium, and barium give more energetic bases than magnesium, zinc, and cadmium. Such are **scandium**, **yttrium**, and **lanthanum**, the atomic weights of which are greater than those of Ca , Sr , and Ba , and which give ordinary oxides of the composition R_2O_3 , and are subject to the periodic grouping of the elements in all other respects. However, they are accompanied in nature by a whole series of other elements among which **cerium**, $Ce=140$, and **thorium**, $Th=232$, must be referred to group IV., but which all have so many points in common that they have long been classed under a special group of **elements of the rare earths**, so called from the comparative rarity of the minerals from which they are extracted and from the fact that their saline oxides of the composition R_2O_3 and RO_2 are analogous to such earths as CaO and Al_2O_3 . The best known, besides the five above-mentioned elements (Sc , Y , La , Ce , and Th) which have their corresponding places in the periodic system, are **ytterbium** $Yb=173$, which apparently has its proper place in group III. in the 10th series, then praseodymium, $Pr=141$ and neodymium, $Nd=144$, one of which apparently belongs to group V. and the 8th series. The other elements of the rare earths are hardly known in a pure form, and if their basic oxides be given the composition R_2O_3 they should belong to group III. It seems to me that new and more complete researches are necessary before any true judgment can be formed about these elements. The great authority on these elements, Professor **B. F. Brauner**, of Prague, has at my request written a special description of them for this book, and I am happy to be able to embellish my work with his concise

but detailed account of these metals of the rare earths. The metal cerium is treated with the rest, although, like thorium, it strictly belongs to group IV.

THE ELEMENTS OF THE RARE EARTHS.

PROF. B. BRAUNER.

The discovery of the rare earths.—In 1794 Gadolin discovered a new earth or oxide, which Ekkeber named *yttria*, the mineral now known as gadolinite occurring at Ytterbi, near Stockholm. In 1803 Berzelius and Gisinger, and at the same time Klaproth, discovered a new oxide, which the Swedish chemist named a 'cerium earth,' in cerite, or the 'heavy stone of Bastenaus.' In 1839 Mozander found that it contained *lanthanum*, and in 1842 he found that this lanthanum, which gives colourless salts, contains an earth forming rose-coloured salts, which was named oxide of didymium. In 1843 Mozander decomposed yttria into three different earths by a method of fractional precipitation with ammonia and acid oxalate of potassium.

The first gives colourless salts and retained the name of yttria; the second gave pink salts and was called the oxide of terbium; and the third, which gave a dark-yellow peroxide and colourless salts, was called erbia. In the beginning of the sixties Berlin, and a little later Bar and Bunsen, found that the acid mixture formerly called yttria contained, besides Mozander's yttria, yet another earth forming pink salts, which they named erbia. And when after this Delafontaine found a third yellow earth in Mozander's earth, it was called terbia.

More recent researches have led to the discovery of a whole series of oxides of new elements in the gadolinite earths. Thus Delafontaine's phillipium (which Roscoe thought a mixture) and decipium (1878) partly correspond with samarium discovered in 1879 by Lecoq de Boisbaudran in the didymium obtained from Samarskite, and Smith's mozandrium with terbium. In 1878 Marignac investigated the oxide of erbium discovered by Bar and Bunsen and separated from it a white earth giving colourless salts and containing an element he named ytterbium. At the same time Soret also discovered a new element in oxide of erbium which he called X. In 1879 Nilson confirmed the existence of the ytterbium discovered by Marignac, and split up the oxide then known as oxide of ytterbium into the true oxide of ytterbium and a new earth whose element he called scandium. In 1879 Clève showed that the oxide, which was then known as oxide of erbium, in reality consists of three earths. One of these contains the element holmium, which resembles Soret's X, another pure erbium, and the third thulium. In 1886 Lecoq de Boisbaudran showed that oxide of holmium also contains oxide of dysprosium.

In 1880 Marignac investigated the earths of samarskite and discovered two new earths in them, the oxides of $Y\alpha$ and $Y\beta$. In 1886 the oxide of $Y\alpha$ was termed 'gadolinitia.' The oxides of $Y\beta$ proved to be identical with the samarium of Lecoq. In 1901 Demarcay separated a new oxide from samarium, forming colourless salts whose element he called 'europium.'

The researches of Delafontaine, Clève, and Brauner in the eighties showed that the element then known as didymium consisted of several elements, and that portions of the absorption bands of the former didymium corresponded to each of these elements. At the same time Brauner and Clève separated samarium from the didymium of cerite. In 1882 Brauner also showed that the lanthanum of cerite consists of a mixture of two elements. In 1885, Auër von Welsbach succeeded in ultimately decomposing didymium into praseodymium, giving green salts, and neodymium, giving rose-coloured salts. The most recent researches of Crookes, Krüss, Nilson, Demarçay, and others apparently show that neodymium consists of a mixture of several elements. Furthermore, Krüss and his assistants showed that the oxides of erbium, holmium, and terbium consist of several very similar earths. An investigation of the spectra of phosphorescence given by several of these rare earths under the action of an electric discharge *in vacuo* (or else by the action of cathodic or dark radiation) led Crookes to the conclusion that the former oxide of yttrium contained several new elements. Lecoq de Boisbaudran (1885) is not of this opinion, and thinks that holmium, terbium, and samarium contain yet other new elements. One of these is europium, discovered by Demarçay.

The occurrence of the rare earths in nature.—They are only found in compounds forming rather rare minerals. In some of these minerals the cerite earths (see later), designated by [Ce] in the context, predominate, while in others the yttrium earths subsequently designated by [Y] predominate, but frequently both these earths occur simultaneously. Over fifty minerals containing the rare elements are known. We shall only enumerate the chief of these. *Silicates*: [Ce], cerite, orthite, allanite; [Y], gadolinite, yttrialite; [Ce, Y], tritohite. *Carbonates*: [Ce], lanthanite; and containing fluorine, parasite, samarskite. *Phosphates*: [Ce], monazite (containing Th), rhabdophane [Y], xenotime. *Fluorides*: [Ce], fluorcerite; [Y], yttrioerite. *Silico-titanites*: [Ce], cheokinite, mosandrite; [Y], keilhauite. *Titano-niobium compounds*: [Ce], aeschynite, pyrochlore. *Tantalo-niobium compounds*: [Y], sipphilit, tyrite, yttrio-tantalite, samarskite, euxenite; [Y, Ce], fergusonite (contains He), eueite, bröggerite, and nivenite, besides the rare earths, contain uranium, thorium, lead, and also, like some of the above minerals, helium. Besides these, the rare earths occur in small quantities in many minerals, such as apatite, strontianite, and serpentine; in eoprolites, in the ash of tobacco and bones, and in urine (Cossa). When Auër showed that a mixture of the oxides of thorium and cerium may be employed in incandescent lamps for lighting purposes, the rare earths were sought for in different localities, and a source for their exploitation was found in the comparatively larger deposits of monazite occurring in Brazil and North Carolina, and this has given the possibility of extending our knowledge of the rare earths in recent years. The lines of Y, Er, and La, and perhaps Ce, have been detected in the solar spectrum.

The atomic composition of the rare earths.—Prior to the close of the sixties it was held that the rare earths which exhibit clearly basic properties (this chiefly refers to the oxide of lanthanum, the hydrate of the suboxide of cerium, and the oxides of yttrium, erbium, and didymium then known)

form compounds of the type RO like the oxides of the metals of the alkaline earths. The higher oxide of cerium was then given the formula Ce_3O_4 , like the compounds Mn_3O_4 and Fe_3O_4 . According to their analogies and types RO, the following atomic weights were ascribed to the metals of the rare earths : Y = 61.7, Ce = 92, La = 90-94, Di = 95, Er = 112.7—that is, they were considered to be divalent with respect to hydrogen. After having established his periodic system, Mendeléeff (1870) observed that the elements of the rare earths do not fit into the general order of the elements if the above atomic weights are adopted, and that if the higher oxide of cerium be regarded as a compound of two oxides, CeO , Ce_2O_3 , account must be rendered of the fact that one of these oxides, namely, Ce_2O_3 , and its corresponding salts are not obtainable. As the amounts of oxygen in the two known oxides of cerium (CeO and Ce_3O_4 , if $\text{Ce} = 92$) are in the ratio 3 : 4, Mendeléeff proposed the formulæ Ce_2O_3 and Ce_2O_4 or CeO_2 for the two oxides. In this case the true atomic weight of cerium would be three times the hydrogen equivalent, $46 \times 3 = 138$, and then this element would find a place in group IV., in the 8th series ; the properties of cerium and its compounds were found to correspond with such a position among the other elements.

Mendeléeff even foresaw a higher atomic weight, about 140, for pure cerium, and also the possibility of the existence of CeF_4 ; and Brauner's subsequent researches entirely confirm his prediction. Moreover, Mendeléeff determined the specific heat of metallic cerium, and found it to be equal to 0.05, which, multiplied by the new atomic weight, is equal to 6.9, or very nearly the normal atomic specific heat. Hillebrand (1876) made fresh determinations, and obtained a value 0.0448, which gives the atomic specific heat 6.3. With respect to didymium and lanthanum, Mendeléeff could not arrive at a decisive conclusion, as only *one* element with an atomic weight of about 140 could be conveniently placed in group III. (oxide of type R_2O_3). He therefore considered it possible to accept the formulæ of the oxides as R_2O_3 for one, and RO_2 for the other of these elements. Subsequently Mendeléeff adopted the type R_2O_3 for the oxides of both metals, and only placed lanthanum in his system by the side of Ce. For the little investigated elements Y and Er, Mendeléeff (1870) adopted the atomic weights : Y = 88 and Er = about 178, and gave them the positions III., 6 and III., 10 in his periodic system. The researches of Clève and Höglund (1873) on yttrium and erbium, of Clève (1874) on yttrium, erbium, didymium, and lanthanum, of Tolin (1875) on cerium, and Hillebrand (1876) on the specific heats of Ce, La, and Di, showed the atomic weight of La to be 138-139, and that of Di 144, the formulæ of the oxides being La_2O_3 and Di_2O_3 .

Subsequently, Marignac, Clève, Nilson, Krüss, Brauner, and their assistants, Jones, von Scheele, Benedix, Muthmann and his assistants, Coppel, and others, investigated the elements of the rare earths, and their researches still further confirmed Mendeléeff's views, so that the composition of the chief basic oxides or earths is now expressed by the formula R_2O_3 . Thus one chief common type RX_3 is accepted for the elements of the rare earths. The higher existing oxides of Ce, Pr, and Nd are given the formula R_2O_4 , that is, they are looked upon as compounds of the type RX_1 . Although the vapour density of none of the compounds of the metals of the rare earths is known

(owing to their not being volatile), still other physical data have been obtained, besides the specific heats of Ce, La, and Di (or, more strictly speaking, of the mixture of Pr and Nd) and give the requisite means for determining the atomic composition of the compounds of these elements.

The boiling-points of their solutions (Chap. VII., laws of Raoult and van't Hoff) confirm the molecular compositions CeCl_3 (Muthmann), PrCl_3 (Brauner), and NdCl_3 (Matignon). But the atomic weights of the remaining elements of the rare earths can as yet only be judged by analogy by studying the composition of corresponding salts, such as the chlorides, sulphates, and nitrates, &c., according to the researches of Clève, of the double platinum salts according to Nilson, of the double sulphates of cerium according to Brauner, and of the acid sulphates also according to Brauner.¹

Another important reason for taking the composition of the oxides as R_2O_3 is the isomorphism of the monoclinic sulphates of yttrium, praseodymium, neodymium, samarium, terbium, erbium, and ytterbium, of the composition $\text{R}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$. Moreover, the corresponding sulphate of cerium crystallises in the rhombic system, and is not isomorphous with the preceding salts, and the sulphates of scandium and lanthanum do not give hydrates with $8\text{H}_2\text{O}$, but with $6\text{H}_2\text{O}$ and $9\text{H}_2\text{O}$ respectively. Further, the values expressing the solubilities of the oxalates in a normal solution of sulphuric acid (i.e., one containing 49 grms. of H_2SO_4 per litre of water), and in a solution of ammonium oxalate are of the same order for those of the above elements which give R_2O_3 and for other compounds known to belong to the type RX_3 , whilst the corresponding solubility for thorium compounds of the type RX_4 is of quite another order.

The position occupied by these elements in the periodic system gives a means for testing the truth of the atomic weights of scandium and yttrium (besides those of lanthanum and cerium, which have been firmly established on the basis of physico-chemical data; but for the remaining elements there are no physico-chemical data for forming any conclusion in this respect, as mentioned at the end of this chapter).

Characteristic properties and reactions.—The elements of the rare earths not only occur together in nature, but they also closely resemble each other in their chemical relations. The only ones which have been obtained in a free metallic state are Ce, La, Nd, and Y, prepared by the electrolysis of their chlorides, or in a less pure form by the action of Na on their chlorides or of Mg on their oxides. If they are reduced from their oxides in a stream of hydrogen they form hydrides in the form of a black powder. The metals remain unaltered in dry air, but easily become oxidised in damp air, especially if the temperature be raised. In the form of powder they burn with a brilliant light. The oxides of the form R_2O_3 are mostly somewhat powerful bases, but the basic properties of La_2O_3 and Y_2O_3 (they combine directly with water and readily absorb CO_2 from the air)

¹ Great caution is required in drawing such conclusions 'by analogy,' as it is easy to fall into error. For instance, while the atomic weight of beryllium appeared yet doubtful, Nilson and Pottersen cited the analogy of many of the salts of oxide of beryllium and of alumina as a proof that $\text{Be} = 13.6$, and that its oxide was Be_2O_3 . Now it is known that this apparent analogy proceeds from the fact that beryllium forms a link between groups II. and III.

are much more energetic than those of Yb_2O_3 and Se_2O_3 . With the exception of CeO_2 , Yb_2O_3 , and Se_2O_3 , they all dissolve easily in cold acids and evolve much heat in so doing. The anhydrous sulphates, $\text{R}_2(\text{SO}_4)_3$, are readily soluble in ice-cold water and easily give supersaturated solutions. At a somewhat higher temperature these solutions deposit hydrated sulphates which dissolve with difficulty in cold water, and are still less soluble in hot water. The chlorides, RCl_3 , bromides, RBr_3 , and iodides, RI_3 , are very hygroscopic and readily soluble in water. The same may be said of the nitrates, $\text{R}(\text{NO}_3)_3$. The fluorides, RF_3 , are insoluble in water, as also are the carbonates and phosphates. The sulphides, R_2S_3 , decompose in dissolving in water, and form a hydroxide, $\text{R}(\text{OH})_3$, and H_2S . Carbides are formed when the oxides are heated with carbon in the electric furnace. The carbides, when treated with water, give a mixture of acetylene, ethylene, methane, and other gaseous, liquid, and solid hydrocarbons (Moissan and others).

Aqueous solutions of the salts of the rare earths are not precipitated by H_2S . With ammonia they give amorphous precipitates of basic salts. Caustic soda precipitates the hydroxides, which readily absorb CO_2 from the air and are insoluble in an excess of alkali. Sulphide of ammonia acts like free ammonia. The carbonates of the alkali metals precipitate amorphous carbonates. Powerful bases (like La_2O_3) are insoluble in an excess of the reagent; but the less energetic the basic properties, the greater is the facility with which they are dissolved by an excess of the carbonate of the alkali metal. Carbonate of ammonium is a better solvent than carbonate of potassium. Oxalic acid and the oxalates give voluminous precipitates having the composition $\text{R}_2(\text{C}_2\text{O}_4)_3 \cdot x\text{H}_2\text{O}$, which after a time become crystalline. These precipitates are but slightly soluble in the mineral acids, but as a rule, the more soluble they are the greater is the energy of the base. They dissolve feebly in an excess of oxalate of ammonium, but generally speaking the solubility increases as the base becomes weaker. With peroxide of hydrogen in the presence of alkalis, they give precipitates of hydrated peroxides, $\text{R}_2\text{O}_5 \cdot x\text{H}_2\text{O}$, which as a rule are of the same colour as the hydroxides. Only the salts of cerium give a hydrated peroxide $\text{CeO}_3 \cdot x\text{H}_2\text{O}$ of the same colour as hydrated oxide of iron. All the sulphates of this group form, with sulphate of potassium, double salts, having mostly the composition $3\text{K}_2\text{SO}_4 \cdot \text{R}_2(\text{SO}_4)_3$. *These elements are divided into two groups according to the solubility or insolubility in a solution of sulphate of potassium.* The double sulphates of the *cerite metals* are quite insoluble or dissolve with difficulty in a saturated solution of K_2SO_4 . These include La, Ce, Pr, Nd, Sm, Eu, and Se. The double sulphates of *potassium and the gadolinite metals* are more easily, or even very, soluble in a saturated solution of K_2SO_4 . These include Y, Gd, Tb, and Yb, and the mixtures known as holmium, erbium, and thulium. The formates of the cerite metals also dissolve with difficulty in water; while the same salts of the gadolinite elements, i.e., the analogues of yttrium, are easily soluble. Benedix showed that the platino-cyanides of the cerite metals crystallise in yellow crystals with a blue metallic lustre. The platino-cyanides of the yttrium metals are cherry-coloured, with a green metallic lustre. In the colour and form of its platino-cyanides, gadolinium belongs to the yttrium elements.

Cerium and praseodymium form two kinds of oxides. The lower corresponds to the other rare earths in its form, R_2O_3 . The higher oxides of cerium and praseodymium are formed after the type R_2O_4 . They form salts of the type RX_3 , but those of praseodymium are very unstable. The oxides, R_2O_4 , of cerium and praseodymium are obtained by fusing their nitrates with nitre, and the oxide Ce_2O_4 is also obtained by calcining the oxalates and sulphates of the lower form CeX_3 . The hydroxide of the higher oxide of cerium, $Ce(OH)_4$, is a much weaker base than $Ce(OH)_3$. The former is obtained by the action of chlorine on $Ce(OH)_3$ in the presence of caustic potash. The salts of the higher form, CeX_4 , are yellow, orange-yellow, and brownish-yellow in colour and form yellow solutions with a small amount of water, but hydrolytic decomposition takes place in the presence of a larger amount of water and basic salts are precipitated. Alkalies precipitate the hydroxides or basic salts from these solutions. Carbonate of ammonium gives a yellow precipitate soluble in an excess of the reagent. The addition of peroxide of hydrogen causes the solution to become red, and a corresponding double salt of potassium and peroxide of cerium is formed. Atmospheric oxygen acts like H_2O_2 , only more slowly. In acid solutions, reducing agents, such as sulphurous acid, oxalic acid, ferrous salts, H_2O_2 , &c., convert the yellow salts of the higher oxide of cerium, CeX_4 , into colourless salts of the lower form, CeX_3 , and potassium permanganate or persulphate converts CeX_3 into CeX_4 .²

It follows, therefore, that, in distinction from all the other metals of the rare earths (excepting thorium) forming oxides R_2O_3 and salts RX_3 , only cerium gives a still higher oxide, CeO_2 , and corresponding salts, CeX_4 . In this respect the as yet little known praseodymium approaches cerium (Brauner).

Owing to the great similarity in their properties and reactions, the separation and distinction of the rare earths from each other have many peculiarities. The following methods are employed for distinguishing them from each other.⁴³ **The method of determining their atomic weights.** The oxides of the type R_2O_3 , obtained by igniting the oxalates, are weighed, dissolved in nitric acid, and mixed with a small excess of sulphuric acid, evaporated, and heated to 600° to drive off the excess of acid. The sulphates of such powerful bases as La_2O_3 are able to withstand this high temperature, whilst those of the weaker bases are decomposed at a temperature of 440° with the partial formation of basic salts. This method of determining the atomic weights (strictly speaking equivalents) was repeatedly used and was the source of those errors which were discovered by Brauner and Pavlichek, and which proceed from the possibility of the formation, under these conditions, not only of the neutral salt, $R_2(SO_4)_3$, but also of the acid salt, $R_2(SO_4)_3 \cdot 3H_2SO_4$, which lowers the atomic weight. But the true atomic weight may be calculated (Brauner and Pavlichek) from that given by this method, either by determining the amount of sulphuric acid (by titration), or by calcining until the basic salt begins to be formed and then determining the weight of SO_3 wanting. If the basic properties of the R_2O_3 under investigation be weaker, the anhydrous sulphate may be first obtained by heating to 440° ,

² The hydrate of cerium peroxide, CeO_2 , is formed not only by H_2O_2 in the presence of alkalies, but also in the presence of the acetates of the alkali metals.

and thus converted into the oxide R_2O_3 by strongly igniting it. In the case of cerium (and also thorium), the oxide R_2O_4 is obtained in this manner (Brauner, Nilson, Krüss). The determination of the atomic weight not only forms an important distinguishing feature for each separate element, but also gives, from the variation of the values obtained at different stages of the separation, a means for following the course of separation and purification in the fractional treatment of a mixture of two or more mixed oxides.

2. **The luminous spectra of electric sparks.**—If the sparks from a large induction coil connected with Leyden jars be caused to pass between carbon or platinum electrodes moistened with a solution of one of the chlorides of this group, and be examined through the spectroscope, it will be found that each element gives its characteristic spectrum with a large number of lines, which render it possible, not only to determine the element, but also to indicate its degree of separation and purity. The spectra of the metals of the rare earths have been tabulated by Thalén, Bunsen, Lecoq de Boisbaudran, Brauner, Auër, Hartley, Demarçay, and Crookes.

3. **Absorption spectra.**—In 1858 Gladstone discovered that when white light is passed through a solution of didymium salt into the spectroscope it gives an absorption spectrum with many dark bands. Later, Delafontaine, Bar and Bunsen, Thalén, Lecoq de Boisbaudran, Brauner, Krüss and Nilson, Crookes, Demarçay, Auër von Welsbach, Becquerel, Urbain, Muthmann, Forsling, and others investigated the absorption spectra of solutions of all the rare earths. It has already been mentioned that the composite compositions of the former didymium and erbium, and the elements praseodymium, neodymium, samarium, &c., were discovered by this means. Soret finds that some colourless salts which do not yield simple absorption spectra exhibit characteristic absorption lines in the ultra-violet portions of their spectra. The investigation of absorption spectra is particularly important and useful in separating and purifying the earths, but it must be borne in mind that the position and intensity of the bands vary with solutions of *one and the same earth* according to the concentration of the solution, the nature of the acid radicle, and the amount of free acid.

4. **Special luminous linear spectra** which sometimes differ from the ordinary spark spectra are obtained, according to Lecoq de Boisbaudran, if the positive pole of the Ruhmkorff coil be immersed in the solution of a chloride, and the negative pole be fixed directly over the surface of the liquid. The spectra obtained in this manner resemble Crookes's spectra of phosphorescence. The existence of the new elements, holmium, terbium, and samarium, was indicated by this method.

5. **Spectra of phosphorescence and cathodic radiation.**—In 1883 Crookes observed that the basic sulphates of certain rare earths, or even the earths themselves, become phosphorescent when they are subjected to the actions of an electric discharge in an almost perfect vacuum, and that the light so obtained gives spectra with characteristic bands. Crookes thought that he had obtained several elements by fractional decomposition from the old yttrium, and that he had thus discovered the existence of several elements which were apparently analogous to those found by Lecoq de Boisbaudran by the above method. It was afterwards seen that these spectra are extremely

sensitive; that the smallest traces of a foreign substance act on them, so that the conclusions drawn from them by Crookes, Lecoq de Boisbaudran, and others were not generally accepted; for instance, Lecoq says that pure yttrium does not give spectra of phosphorescence. Bettendorf and also Muthmann and Baur subsequently occupied themselves with this subject. The results of their researches in general confirm those obtained by Crookes, but differ from them in details. This method also proved most important for testing the gradual separation of the rare earths from each other. More recently (1901), Baur and Mare found that the oxides or salts of yttrium, gadolinium, and lanthanum do not give broken spectra *when pure*. The spectra previously observed for these elements were due to the presence of small amounts of erbium, neodymium, and praseodymium. This shows that the conclusions drawn from this class of data are still subject to some doubt.

6. **Spectra of radiation from the incandescent earths.**—Bar and Bunsen found that when the earth of erbium is heated to incandescence it emits an intense light, the spectrum of which exhibits light bands corresponding in position with the dark absorption bands. The intensity of the light is increased by the addition of phosphoric acid, but the position of the bands remains unchanged. Oxide of didymium exhibits the same phenomenon, but only with respect to its neodymium constituent. The addition of oxide of erbium and other oxides entirely changes the spectrum. The oxides of samarium and holmium also emit a discontinuous light when heated to incandescence.

Treatment of the minerals for the extraction of the rare earths.—Formerly the cerite earths were almost exclusively extracted from cerite from Bastenaus. This is finely powdered and mixed with strong sulphuric acid. The mixture becomes heated and forms a friable grey powder, which is heated to drive off the excess of sulphuric acid and to decompose the sulphate of iron. The residue is dissolved in chlorine water, and the heavy metals precipitated by hydrogen sulphide, any iron remaining being oxidised with chlorine and hydrochloric acid then added. The solution is then heated and the rare earths are precipitated in the form of oxalates by means of oxalic acid. Auër von Welsbach reduces cerite to a coarse powder, calcines it, treats it with strong hydrochloric acid over a hot water-bath, and evaporates to dryness. The oxalates are precipitated at 50° , well washed, and converted into oxides by igniting in an iron dish.

At the present time about 50–60 per cent. of the cerite oxides and 1–5 per cent. of the yttrium oxides are obtained in the extraction of oxides of thorium from American monazite, which contains about 1–8 per cent. of the thorium earth (ThO_2). The rare earths are here obtained as a by-product or residue, so that impure cerite oxides can now be procured for research in any quantity at a low price.

Gadolinite is the chief source of the gadolinite or yttrium earths. The finely ground mineral is treated with hydrochloric acid, heated, and evaporated. The residue is treated with water and precipitated with oxalic acid. The precipitated salts are washed and ignited with access of air. Euxenite and fergusonite are decomposed by fusing with KHSO_4 , and the solution poured off from the precipitate of tantallic and niobic acids. Oxalic acid is

added to the solution. Samarskite is decomposed with hydrofluoric acid, evaporated, and the residue treated with sulphuric acid, and the aqueous solution precipitated with oxalic acid.

THE SEPARATION OF THE RARE EARTHS.

A. *Separation of cerium*.—Cerium is separated first, in treating a mixture of the rare earths, owing to the ease with which the compounds CeX_3 pass into CeX_4 . (1) In the treatment of the *crude yttrium earths* they are dissolved in nitric acid, evaporated, and the nitrates then fused to incipient decomposition. This is done because $Ce(NO_3)_2$ decomposes with the formation of insoluble CeO_2 at temperatures at which the nitrates of the other rare earths remain unchanged, so that they can be extracted by water. (2) In the case of the *crude cerite earths* their oxalates are calcined. A dark reddish-brown powder is obtained, consisting of CeO_2 , La_2O_3 , the higher oxides of praseodymium and neodymium, together with a small amount of other oxides, and this is dissolved in nitric acid. The separation of the cerium is based upon the fact that water decomposes the salts of the form RX_4 , with the formation of insoluble basic salts. The excess of nitric acid is driven off by evaporation from the nitrates, which are then dissolved in a small quantity of cold water. The solution is decanted into a larger quantity of boiling water.³ The basic salt of the higher oxide of cerium then separates out; it still retains the constituents of didymium, as the latter are also partly converted into salts of the form RX_4 . To obtain pure cerium salts, this basic sulphate must be dissolved in sulphuric (Bunsen) or nitric (Brauner) acid and the precipitation with hot water repeated several times. The filtrates from the precipitates of cerium contain some reduced CeX_3 , besides other earths of the form RX_3 . The CeX_3 is removed by precipitation in the form of oxalate, or by igniting the oxides, dissolving in nitric acid and precipitating CeX_4 by boiling with magnesite (Bunsen), or by Debray's process, which is described later. (3) Cerium may be separated from the other earths by obtaining the oxide CeO_2 from the oxalate in that portion of the solution which contains CeX_4 and boiling it with the remaining solution. The basic salt $CeO_2(CeX_4)_4$ is precipitated (Auër von Welsbach). (4) Cerium salts of the type CeX_4 when mixed with nitrate of ammonium and nitric acid first crystallise out in the form of a double salt $Ce(NO_3)_4 \cdot 2NH_4NO_3$. The pure cerium salt is obtained by repeating the process (Auër von Welsbach). (5) Debray fuses the impure nitrate of cerium with eight parts of nitrate of potassium at $300-350^\circ$, when only nitrate of cerium is decomposed with the formation of CeO_2 . The cerium may be further purified by repeating the process. (6) Mozander precipitates a mixed solution of RCl_3 with an excess of caustic potash and passes chlorine through the solution; CeO_2 is precipitated in the form of hydroxide, but it still retains some praseodymium. A pure salt of Ce is obtained by repeating

³ According to Bunsen this water is slightly acidulated with sulphuric acid. Brauner does not add any sulphuric acid. Wyrouboff and Verneuil add ammonium nitrate to the solution.

the process about six times. (7) Poppe adds sodium acetate to a neutral solution of RCl_3 and precipitates the Ce as $\text{Ce}(\text{OH})_3$ with chlorine or KOCCl . (8) Stolba treats a solution of the impure cerite oxides with KMnO_4 in the presence of $\text{Zn}(\text{OH})_2$, which gives a precipitate of impure oxide of cerium. If the RCl_3 and KMnO_4 be taken with oxide of mercury, then praseodymium and neodymium are also precipitated with the cerium, while lanthanum remains in solution (Winkler). (9) According to Gibbs, the cerium in a mixture of nitrates is first oxidised by boiling with PbO_2 and nitric acid, after which the solution is decomposed with water and the cerium precipitated. (10) The chromates of the rare metals are heated to 110° , only the cerium salt being decomposed at this temperature (Pattinson and Clark). (11) Wyruboff precipitates the cerium salt in the presence of nitrate or sulphate of ammonium and the cerium remaining in the filtrate with persulphate of ammonium and acetate of sodium. (12) Meyer and Koss separate the cerium, fused with magnesium acetate, by means of peroxide of hydrogen. The hydrate of peroxide of cerium, CeO_2 , is then transformed into $\text{Ce}(\text{OH})_4$ by boiling.

In all the preceding methods the separation is based upon qualitative differences between the salts CeX_3 and those of the other earths, RX_3 . The same principle may be applied to praseodymium. To separate praseodymium from lanthanum, their nitrates are fused with nitre at $400\text{--}430^\circ$. Only the nitrate of praseodymium is decomposed and separated as Pr_2O_3 (Brauner).

B. *Separation of the remaining rare earths of the type RX_3 from each other.*—This is done in several ways. (1) By means of K_2SO_4 . The cerite earths form with K_2SO_4 double salts which are insoluble in a saturated solution of the sulphate, whilst the double sulphates of the yttrium earths are soluble. This classical method does not, however, admit of the perfect separation of the two groups, because the solubility is a purely relative factor, which in the case of yttrium attains a maximum of 4.9 grms. Y_2O_3 per 100 vols. of saturated solution of K_2SO_4 . Thus, in a mixture of the earths of the two groups, the cerite earths are partially dissolved, while a portion of the yttrium earths remains undissolved. Supersaturated solutions are also easily obtained. Marignac dissolved the double sulphates by a fractional method in a solution of K_2SO_4 , and by repeating the process separated the elements $\text{Y}\alpha$ (gadolinium) and $\text{Y}\beta$ (samarium). Lecoq carried on a fractional separation by precipitating solutions of the sulphates of the earths with K_2SO_4 and alcohol, and succeeded in separating the elements Tb, Dy, Ho, and Er in this way. (2) The *formates* of the cerite earths dissolve with difficulty in water, while those of the gadolinite (yttrium) earths are more easily or even very easily soluble. This method has the inconvenience of easily forming supersaturated solutions. Crystallisation of the acetates sometimes gives the same results (Brauner). (3) Urbain took advantage of the unequal solubility of the aceto-acetic salts and ethyl-sulphonic compounds for separating the rare earths from each other. (4) The *double ammonium nitrates* were first employed by Mendeléeff (1873) for separating lanthanum from didymium. The salt of didymium is the first to crystallise out from a mixture containing both earths. Auër von Welsbach took a

similar solution and decomposed the didymium into praseodymium, the double salt of which crystallises out with the double salt of lanthanum, and neodymium, the double salt which remains in the mother liquor. The process of crystallisation must be repeated several times. The neodymium is ultimately recrystallised in the form of a less soluble double salt of sodium, or of sodium and ammonium. As a rule the weaker the basic properties of the earth, the greater the facility with which its double salts dissolve. Demarçay employed the double nitrates of magnesium for separating europium, and also recrystallised the nitrates from strong nitric acid. (5) Mozander took advantage of the difference in solubility in water of the hydrated sulphates for separating lanthanum from didymium. A solution of the anhydrous salts in six parts of ice-cold water deposits chiefly the salt $\text{La}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$, when heated to 35° . This process must be frequently repeated, but it is not so good as the Mendeléeff-Auër method. (6) When the oxides (hydroxides) of the earths are heated in a solution of NH_4NO_3 the most powerful base passes into solution to the greatest extent (Marignac, Brauner). (7) The hydroxides are treated by heating in ammonium carbonate solution and the solution then precipitated fractionally with acetic acid. (8) The difference in solubility of the chromates in K_2CrO_4 solution is taken advantage of for separating the earths from each other. (9) *Crystallisation* of a solution of the oxalates in potassium oxalate, the salts of the weakest bases being the most soluble. (10) Decomposition of the nitrates by ignition (Marignac, Berlin, Bar and Bunsen). The nitrates of the weakest bases are more easily decomposed than those of the more energetic bases. But the difference is purely a relative one and the process must be repeated many hundreds of times. Bar and Bunsen separated yttrium and erbium, and Marignac terbium and ytterbium, while Nilson separated scandium from ytterbium, and Clève further decomposed erbium in this manner. In order to separate the cerite earths from each other, Schutzenberger fused their nitrates with nitre, as did Debray (see A, 5). (11) *Fractional precipitation*: (a) by *ammonia* with a mixed solution of the earths. Ammonia first gives a precipitate in which the more feeble bases predominate, while the more energetic bases remain in solution. Several of the earths were obtained pure or were further split up by this method. (b) Caustic potash, magnesia, or an alcoholic solution of aniline may be used instead of ammonia, or even a mixture of the earths themselves may be partly employed as a precipitant after being precipitated with oxalic acid and ignited. (c) *Oxalic acid*. As a rule the earths having the weakest basic properties are concentrated in the first precipitates. Treatment of the oxalates with mineral acids forms a modification of this method. The process of fractional precipitation must be repeated very many times. (12) The application of fractional electrolysis to the separation of the rare earths presents some interest.

As regards the *classification of the elements* of the rare earths and their places in the periodic system, it can now be confidently affirmed that scandium, yttrium, and lanthanum belong to the even series of the third group, as they should do, according to their atomic weights and the volumes of their oxides.

Position	III., 4	III., 6	III., 8
Element	Sc	Y	La
Atomic weight	44	89	139
Volume of R_2O_3	35	45	50

The other elements of the rare earths probably form an inter-periodic group or node in the system, in which they follow each other according to the value of their atomic weights.

Scandium, $Se = 44.1$ (Nilson).—The discovery of this element in 1879 by Nilson is of particular interest, because its existence and even its properties were predicted by Mendeléeff in 1871 for ekaboron, which was wanting in the periodic system. This prediction was confirmed in a most brilliant manner, for the atomic weight, 44, was found as predicted; further, the specific gravity of the oxide (predicted 3.5, actual 3.8) and the composition and feeble basic character of its oxide, $Eb_2O_3 = Sc_2O_3$, the difference in the structure of its double salts with sulphate of potassium from that of the alums, and a whole series of other properties and reactions belonging to it as a lower atomic analogue of yttrium, all proved to be identical with those predicted by Mendeléeff. The oxide, Sc_2O_3 , is a white powder, dissolving slowly in acids. Its salts are colourless and do not give an absorption spectrum. Alkalies precipitate an amorphous hydrate, $Se(OH)_3$, from their solutions. Anhydrous $SeCl_3$ is unknown. The sulphate, $Se_2(SO_4)_3$, crystallises from its solutions with $6H_2O$. Its double salt, $3K_2SO_4 \cdot Sc(SO_4)_3$, is insoluble in a solution of K_2SO_4 . Oxalic acid precipitates the oxalate, $Sc_2(C_2O_4)_3 \cdot 6H_2O$, from solutions as a white finely crystalline precipitate. The spark spectrum of the chloride gives over a hundred lines, some of which are very bright. Pure preparations of scandium are exceedingly rare, as 3–4 kilos of gadolinite or yttrio-titanite only yield 1 gram of oxide of scandium (Clève).

Yttrium, $Y = 89.0$ (Jones).—The element has been obtained as a grey powder having the sp. gr. 3.8 (vol. 23.6) by the action of sodium on YCl_3 and also by electrolysis. It is obtained in an impure form from Y_2O_3 by the action of Mg; but if the mixture is heated in a stream of hydrogen it forms a hydride, Y_2H_3 . The oxide Y_2O_3 is obtained by calcining the sulphate, nitrate, oxalate, &c. It is a white powder, of sp. gr. 5.046 (vol. 45) which easily dissolves in acids. The salts are colourless and do not give any absorption spectra. Alkalies precipitate the *hydroxide*, $Y(OH)_3$, from solutions of its salts. Peroxide of hydrogen and ammonia give the hydroxide of the higher oxide Y_4O_9 (more likely Y_2O_5). Chloride of yttrium, YCl_3 , may be obtained, like all the anhydrous chlorides of the elements of this group, either by evaporating a solution of the oxide in hydrochloric acid with chloride of ammonium and igniting the residue, or by the action of chlorine on a mixture of the oxide and carbon at a red heat. It crystallises from solutions as $YCl_3 \cdot 6H_2O$. Fluoride of yttrium, YF_3 , is amorphous and insoluble in water. Y_2S_3 is a yellowish-grey powder, obtained by heating the oxide in the vapour of carbon bisulphide. The anhydrous sulphate, $Y_2(SO_4)_3$, dissolves readily in water (ice-cold) and crystallises out from solutions as a hydrate, $Y_2(SO_4)_3 \cdot 8H_2O$, in monoclinic crystals, which are isomorphous with those of the corresponding salts of Pr, Nd, Sm, Tb, Er, Yb. An *acid salt*, $Y_2(SO_4)_3 \cdot 3H_2SO_4$, is formed by

heating the sulphate with sulphuric acid (Brauner and Picek). The double salts with K_2SO_4 are soluble in a saturated solution of K_2SO_4 . The nitrate, $Y(NO_3)_3 \cdot 6H_2O$, forms beautiful crystals which readily deliquesce. The salts: $YPO_4 \cdot 2H_2O$, $Y_2(CO_3)_3 \cdot 3H_2O$ and the *double platino-cyanide* $Y_2[Pt(CN)_4]_3 \cdot 21H_2O$, have also been studied. A *carbide*, YC_2 , is obtained, when the oxide is heated with carbon in the electric furnace, as a friable partly crystalline mass which yields a large amount of C_2H_2 and some CH_4 , C_2H_4 , and H_2 under the action of water. The *spectrum* of the sparks of the chloride is very bright and particularly characteristic in giving two groups containing numerous lines in the red and orange portions of the spectrum.

Lanthanum, $La = 139.04$ (Brauner).—The purest preparations of lanthanum have been obtained by the combined methods of Mendeléeff, Auër, Debray, Schutzenberger, and by fractional precipitation with caustic potash (Brauner and Pavliehek). It has been obtained in a free state as a grey powder by Mozander by heating $LaCl_3$ with potassium. Hillebrand and Norton obtained it, by the electrolysis of $LaCl_3$, as a dense mass, sp. gr. 6.163, of an iron-grey colour. It easily reacts with dilute halogen acids, and is slowly decomposed by cold, and violently by hot water. A hydride La_2H_3 (?) is formed by heating the oxide with magnesium in a stream of hydrogen. The oxide La_2O_3 is obtained by calcining the oxalate and other salts. It is a white powder which easily dissolves in acids. Its sp. gr is 6.48. It may be slaked with water like lime, forming $La(OH)_3$, which is also precipitated from solutions of the salts by alkalies. It absorbs CO_2 from the air with avidity. With H_2O_2 in the presence of alkalis the salts of lanthanum give a hydrate of the peroxide La_2O_5 . The salts of lanthanum are colourless and give no absorption spectra. They are sweet and astringent to the taste.

Chloride of lanthanum, $LaCl_3$, is obtained by heating its double salts with sal-ammoniac, by heating the oxalate with sal-ammoniac or in a stream of hydrochloric acid gas and by heating the sulphides in a stream of hydrochloric acid gas. The hydrate, $2LaCl_3 \cdot 15H_2O$ ($LaCl_3 \cdot 7H_2O$?), crystallises out from a hydrochloric acid solution. The oxychloride, $LaOCl$, is formed by heating the oxide in a stream of chlorine. $LaF_2 \cdot H_2O$ is obtained as a gelatinous precipitate. La_2S_3 is obtained by heating the oxide in the vapour of CS_2 , or the sulphate in a stream of hydrogen sulphide, and is a yellow powder easily decomposed by water. The anhydrous sulphate, $La_2(SO_4)_3$, is readily soluble in ice-cold water. At ordinary temperatures, $La_2(SO_4)_3 \cdot 9H_2O$ crystallises out from solutions in acute hexagonal prisms, which are isomorphous with the nonhydrated salt of cerium; at 0° the hydrate $La_2(SO_4)_3 \cdot 16H_2O$ crystallises out (Brauner). The double salts with sulphate of potassium are insoluble in a solution of K_2SO_4 . Lustrous needles of the *acid salt*, $La_2(SO_4)_3 \cdot H_2SO_4$, separate out from the solution of the sulphate in sulphuric acid (Brauner). The crystals of the nitrate have the composition $La(NO_3)_3 \cdot 6H_2O$. Its double salt, $La(NO_3)_3 \cdot 2NH_4NO_3 \cdot 4H_2O$, is important for the separation of lanthanum and forms large colourless crystals. The salts: $LaPO_4$, $La_2(CO_3)_3 \cdot 8H_2O$, $LaCl_3 \cdot PtCl_4 \cdot 13H_2O$. $La_2[Pt(CN)_4]_3 \cdot 18H_2O$, &c., have also been studied.

The carbide, LaC_2 , is obtained, by heating the oxide with carbon in the electric furnace, as a crystalline mass, which is decomposed by water, like the

carbide of yttrium. The spectrum of the spark of chloride of lanthanum is very bright and contains many lines, and gives the possibility of detecting the presence of even small traces of lanthanum.

Cerium, $\text{Ce} = 140.2$ (Brauner).—The element was obtained in a metallic state by the action of sodium upon CeCl_3 . Mozander obtained it as a grey powder, Wohler in globules. Winkler obtained not entirely pure cerium from Ce_2O_3 by means of magnesium. Pure metallic cerium was obtained by Norton and Hillebrand, by the electrolysis of fused CeCl_3 , as an iron-grey metal of sp. gr. 6.628: it melts with greater ease than silver, is malleable and ductile, and can be drawn into wires when hot. It keeps well in dry air, becomes coated with oxide in damp air, and burns brightly at a high temperature. It emits sparks when scratched with a file or flint. It enters into reaction with the halogen acids and water like La. A hydride, $\text{Ce}_2\text{H}_4(?)$, is formed by heating the oxide with magnesium in a stream of hydrogen. As already mentioned, cerium forms two basic oxides and one peroxide. Ce_2O_3 is a more energetic base than CeO_2 or Ce_2O_4 .

A. *Compounds of the type CeX_3* .—The lower oxide, Ce_2O_3 , is not really known in a free state, but a hydroxide, $\text{Ce}(\text{OH})_3$, is obtained by precipitating solutions of RX_3 with caustic potash or soda as a white voluminous precipitate, which absorbs oxygen from the air, and first turns lilac-coloured (a hydrate of Ce_2O_3 , Ce_2O_4 is formed) and then yellow owing to the formation of $\text{Ce}(\text{OH})_4$. The corresponding salts, RX_3 , are colourless and have no absorption spectra. They are sweet and astringent to the taste. The chloride, CeCl_3 , is obtained by heating the oxide in the vapour of CCl_4 , and also as a sublimate by burning metallic cerium in a stream of chlorine. A hydrate, $2\text{CeCl}_3 \cdot 15\text{H}_2\text{O}$, crystallises out from a solution of the hydroxide or carbonate in hydrochloric acid. This hydrate is perhaps the same as that obtained by the action of gaseous hydrochloric acid on $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$. The sulphide, Ce_2S_3 , is obtained (like La_2S_3) by burning metallic cerium in the vapours of sulphur or by heating the oxide in hydrogen sulphide. It is a dark-brown amorphous mass. Golden yellow scales of the sulphide are formed by fusing the oxide with sodium pentasulphide and lixivating with water. The anhydrous sulphate, $\text{Ce}_2(\text{SO}_4)_3$, is obtained by heating the hydrated salt to 440° . It is readily soluble in ice-cold water, and crystallises from its solutions at the ordinary temperature as a *hydrate*, $\text{Ce}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$, in rhombic octahedra, and not in the monoclinic system like the octahydrated salts of the other earths. Alcohol precipitates the same octahydrated salt from aqueous solutions. Besides this, sulphate of cerium forms hydrates with $5\text{H}_2\text{O}$, $6\text{H}_2\text{O}$, $9\text{H}_2\text{O}$ (isomorphous with the lanthanum salt) and $12\text{H}_2\text{O}$. The double salt, $3\text{K}_2\text{SO}_4 \cdot \text{Ce}_2(\text{SO}_4)_3$, is insoluble in a solution of K_2SO_4 . A difficultly soluble double salt, $\text{Na}_2\text{SO}_4 \cdot \text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, is also known, which forms very deliquescent crystals. With NH_4NO_3 , it gives a salt, $\text{Ce}(\text{NO}_3)_3 \cdot 2\text{NH}_4\text{NO}_3 \cdot 4\text{H}_2\text{O}$, which is isomorphous with the salt of lanthanum. The phosphate, CePO_4 , is the chief constituent of the mineral monazite. The salts, $\text{Ce}_2(\text{CO}_3)_3 \cdot 5\text{H}_2\text{O}$, platinum chlorides, $2(\text{CeCl}_3 \cdot \text{PtCl}_4) \cdot 27\text{H}_2\text{O}$, and $2(\text{CeCl}_3 \cdot 2\text{PtCl}_4) \cdot 21\text{H}_2\text{O}$, $\text{Ce}[\text{Pt}(\text{CN})_5]_2 \cdot 9\text{H}_2\text{O}$, &c., are also known. The *formate*, $\text{Ce}(\text{CHO}_2)_3$, and *oxalate*, $\text{Ce}_2(\text{C}_2\text{O}_4)_3 \cdot 11\text{H}_2\text{O}$, are only slightly soluble. The *carbide*, CeC_2 , is obtained by heating the oxide CeO_2 with carbon in the electric furnace

(Moissan), and is a reddish-yellow, transparent, crystalline substance. With water it gives a mixture containing 75 per cent. of acetylene and some ethylene, methane, and smaller amounts of solid and liquid hydrocarbons. If there be less carbon than is required to form the carbide, an oxycarbide, $\text{CeC}_2 \cdot 2\text{CeO}_2$, is formed in reddish-brown plates. The composition of the carbide of cerium is the same as those of Al and Th.

B. Compounds of the type CeX_4 .—The higher oxide, CeO_2 or Ce_2O_4 , is obtained by igniting the oxalate, sulphate, nitrate, and other salts as an almost white powder, possessing a slight yellow tint and having the sp. gr. 6.74. It is insoluble in all acids except strong sulphuric acid. It gives colourless regular octahedra when fused with NaCl (sp. gr. 7.3) or borax—sp. gr. 7.4—or K_2SO_4 —sp. gr. 8.0—which are insoluble in any acid. The hydrate, $2\text{CeO}_2 \cdot 3\text{H}_2\text{O}$, is obtained by reacting with chlorine on $\text{Ce}(\text{OH})_3$ and shaking up with KHO. The hydroxides, $\text{Ce}(\text{OH})_4$ and $\text{CeO}(\text{OH})_2$, are also known. The corresponding salts, RX_4 , are yellow or brown, and have strong oxidising properties. *Tetrachloride of cerium*, CeCl_4 , is not known in a pure state. It is evidently present in the brown solution obtained by dissolving $\text{Ce}(\text{OH})_4$ in cold hydrochloric acid. The solution of the hydroxide in methyl alcohol containing hydrochloric acid is more stable. When treated with carbonate of potassium or ammonium it gives very unstable double salts in the form of yellow crystals. Pure double salts of the composition R_2CeCl_6 have been obtained with salts of organic bases, such as pyridine, quinoline, and triethylamine (Coppel). *Tetrafluoride of cerium*, $\text{CeF}_4 \cdot \text{H}_2\text{O}$, is formed by treating $\text{Ce}(\text{OH})_4$ with hydrofluoric acid. It loses water when heated, and at a higher temperature evolves a gas containing free fluorine. A double salt has been obtained with fluoride of potassium, $3\text{KF} \cdot 2\text{CeF}_4 \cdot 2\text{H}_2\text{O}$ (Brauner). The sulphate of the higher oxide of cerium, $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, is easily obtained by dissolving $\text{Ce}(\text{OH})_4$ in dilute sulphuric acid and forms yellow crystals. When CeO_2 is dissolved in hot sulphuric acid, it forms also the sulphate of the trioxide, and the two combine to give a double salt, $\text{Ce}_2(\text{SO}_4)_3 \cdot \text{Ce}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$, in the form of brown hexagonal crystals. These crystals may also be obtained from the two component salts by synthesis, and the salt $\text{Ce}_2(\text{SO}_4)_3$ may be replaced by the salts of La, Pr, Nd, &c. (Brauner). The nitrate, $\text{Ce}(\text{NO}_3)_4$, is unknown in a pure state, and its solution is easily decomposed by water. With the nitrates of the alkali metals it forms double salts of the type $\text{R}_2\text{Ce}(\text{NO}_3)_6$ ($\text{R} = \text{NH}_4, \text{K}, \text{Rb}, \text{Cs}$). The salts of Mg, Zn, Ni, Co, Mn contain $8\text{H}_2\text{O}$.

Peroxide of cerium, CeO_3 .—Its hydroxide is obtained as a precipitate, like $\text{Fe}(\text{OH})_3$, by the addition of H_2O_2 and ammonia to the salts of the lower oxides. When boiled with water it passes into $\text{Ce}(\text{OH})_4$. The peroxide is soluble in KHCO_3 and crystallises from the solution as a double salt, $\text{Ce}_2\text{O}_3(\text{CO}_3)_3 \cdot 4\text{K}_2\text{CO}_3 \cdot 12\text{H}_2\text{O}$, in blood-red crystals (Job).

Praseodymium, Pr, 140.95 (Brauner).—This element has been obtained as a grey powder by the action of magnesium on the oxide. It forms a hydride with hydrogen and a nitride with nitrogen (Matignon).

Praseodymium gives two forms of oxides: Pr_2O_3 and Pr_2O_4 and compounds of them, Pr_4O_7 and $\text{Pr}_{10}\text{O}_{18}$, and also a hydroxide of the peroxide Pr_2O_5 . (a) *The oxide Pr_2O_3 .* When the oxalate or sulphate is strongly ignited it gives

the intermediate oxide, $\text{Pr}_{10}\text{O}_{18}$, which, when strongly ignited in a stream of hydrogen, forms the oxide Pr_2O_3 as a beautiful light-green powder {of sp. gr. 7.07. Pr_2O_3 is readily soluble in acids, and forms bright light-green salts, which give a characteristic absorption spectrum. Praseodymium chloride, PrCl_3 , is obtained by heating the oxalate in a stream of HCl gas, as a beautiful green crystalline mass which is only slightly volatile when heated (Brauner). The *hydrate*, $\text{PrCl}_3 \cdot 7\text{H}_2\text{O}$, crystallises out in deliquescent crystals from a solution of the oxide in hydrochloric acid. The sulphide, Pr_2S_3 , is obtained by heating the sulphate in hydrogen sulphide as a chocolate-coloured mass. The anhydrous sulphate, $\text{Pr}_2(\text{SO}_4)_3$, is easily dissolved in ice-cold water. The hydrate, $\text{Pr}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$, crystallises out from the solution in monoclinic crystals, which are isomorphous with the sulphates of U, Nd, Sm, Tb, and Er. There are also hydrated sulphates with $5\text{H}_2\text{O}$ and $6\text{H}_2\text{O}$. The double salt, $\text{Pr}_2(\text{SO}_4)_3 \cdot 3\text{K}_2\text{SO}_4 \cdot \text{H}_2\text{O}$, is insoluble in a solution of K_2SO_4 . The *acid sulphate*, $3\text{H}_2\text{SO}_4 \cdot \text{Pr}_2(\text{SO}_4)_3$, is obtained by dissolving the neutral salt in warm sulphuric acid; on cooling it separates out in the form of lustrous green silky needles. The nitrate, $\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, forms deliquescent crystals. The double salt, $\text{Pr}(\text{NO}_3)_3 \cdot 2\text{NH}_4\text{NO}_3 \cdot 4\text{H}_2\text{O}$, crystallises in large crystals which deliquesce in moist air. This property is of great importance for separating praseodymium from the other rare earths. Besides these the following salts have been investigated and obtained: $\text{Pr}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}$, $\text{PrCl}_3 \cdot \text{PtCl}_4 \cdot 12\text{H}_2\text{O}$, $\text{Pr}_2[\text{Pt}(\text{CN})_4]_3 \cdot 18\text{H}_2\text{O}$, the *acetate* $\text{Pr}(\text{C}_2\text{H}_3\text{O}_2)_3 \cdot 2\text{H}_2\text{O}$, and the oxalate $\text{Pr}_2(\text{C}_2\text{O}_4)_3 \cdot 11\text{H}_2\text{O}$. A *carbide of praseodymium*, PrC_2 , was obtained by Moissan in the electric furnace from the oxide and carbon, and takes the form of yellow hexagonal plates. It evolves chiefly acetylene under the action of water. (b) The *dioxide*, PrO_2 , is a brownish-black or black powder. It is obtained impure by burning the oxalate in oxygen or air at a red heat (Scheele). It may be obtained in a pure form by fusing the nitrate with nitre at 430° (Brauner): its sp. gr. is 5.98. It is converted into $\text{Pr}_{10}\text{O}_{18}$ ($= 2\text{Pr}_2\text{O}_3 \cdot 3\text{Pr}_2\text{O}_4$) when strongly heated. Although the higher oxide of praseodymium, PrO_2 , like CeO_2 , has its corresponding saline compounds of the type PrX_4 , it is an 'ozone oxide,' for one of its oxygen atoms acts like the oxygen of peroxides. The salts of the type PrX_4 are very unstable; for instance, a solution of PrCl_4 rapidly decomposes into PrCl_3 and free chlorine. This instability is explained by the molecular volumes, the value for Pr_2O_4 being 57.9, and that for Pr_2O_3 , 46.7, giving the very large difference of +11.2 for 1 atom of oxygen. Hence the salts PrX_4 decompose with the evolution of oxygen and ozone. Pr_2O_4 converts CeX_3 into CeX_4 , the salts of suboxide of manganese into those of the dioxide, and give a blue coloration with sulphate of strychnine and a 'catalytic' reduction with peroxide of hydrogen, $\text{Pr}_2\text{O}_4 + 3\text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2 = \text{Pr}_2(\text{SO}_4)_3 + \text{O}_2 + 4\text{H}_2\text{O}$ (Brauner). A hydroxide of the *peroxide*, Pr_2O_5 , is precipitated from the salts, PrX_3 , by peroxide of hydrogen and alkalis. It is a pale-green gelatinous substance which rapidly decomposes with the evolution of oxygen.

Neodymium, Nd = 143.8 (Brauner).—Praseodymium and neodymium are so alike that almost the only means of distinguishing them is by the colour of their salts and a few other physical properties. Also Pr_2O_3 is a somewhat stronger base than Nd_2O_3 . A mixture of them, consisting of about $\frac{1}{3}$ Pr and $\frac{2}{3}$ Nd, was for a

long time regarded as the element didymium, until Auër split it up into two component parts in 1885. Only a few pure compounds of neodymium are known. The corresponding element neodmium was obtained in the free state as a grey powder, by the action of magnesium upon Nd_2O_3 . Neodymium forms three oxides, of which only the lowest one, Nd_2O_3 , gives salts. (a) The *oxide* Nd_2O_3 is obtained by igniting the oxalate. It is a blue powder, readily soluble in acids, and forming beautifully tinted salts of a reddish-lilac or ruby-red colour. The absorption spectrum has more than 20 bands. The chloride, NdCl_3 , is obtained as a rose-coloured crystalline mass by heating the hydroxide in a stream of HCl . The hydrate, $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$, crystallises out from solutions in deliquescent crystals. Nd_2S_3 (obtained like Pr_2S_3) is olive-coloured. The *sulphate* is somewhat soluble in ice-cold water, and deposits a hydrate, $\text{Nd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$, in the form of ruby-red monoclinic crystals, which are isomorphous with the sulphates of Y, Pr, Sm, Tb, Er, and Yb. It forms sparingly soluble double salts with K_2SO_4 and Na_2SO_4 , and with excess of sulphuric acid gives an acid salt, $\text{Nd}_2(\text{SO}_4)_3 \cdot 3\text{H}_2\text{SO}_4$, in the form of bright rose-coloured silky needles. The *nitrate*, $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, yields a double salt, $\text{Nd}(\text{NO}_3)_3 \cdot 2\text{NH}_4\text{NO}_3 \cdot 4\text{H}_2\text{O}$, with NH_4NO_3 . This salt is more soluble in water than the corresponding praseodymium salt. The *carbide of neodmium*, NdC_2 , forms yellow hexagonal plates. It gives the same hydrocarbons as PrC_2 under the action of water. (b) The *dioxide*, NdO_2 , is formed as a light-brown powder by heating the oxalate or nitrate in oxygen. It does not form corresponding salts, but evolves oxygen when acted on by acids, yielding salts NdX_3 . (c) The *peroxide*, Nd_2O_5 , is obtained as a hydrate by the action of peroxide of hydrogen and alkalies on solutions of salts of neodmium. Like Pr it forms a basic acetate, $\text{Nd}_2\text{O}_5 \cdot (\text{C}_2\text{H}_3\text{O}_2)_3(\text{OH}) \cdot \text{H}_2\text{O}$.

Samarium, $\text{Sm} = 148$ (about).—Those compounds of samarium which were discovered by Lecoq in 1879 have not yet been freed from the compounds of europium, so that the oxide gave a somewhat high atomic weight, $\text{Sm} = 150.3$. The metal is not known in the free state. The *oxide*, Sm_2O_3 , is white, and has the sp. gr. 8.35: it forms topaz-yellow salts, the solutions of which give a characteristic absorption spectrum. The chloride, $\text{SmCl}_3 \cdot 6\text{H}_2\text{O}$, is deliquescent. The sulphate, $\text{Sm}_2(\text{SO}_4)_3$, is a yellowish-white powder, its hydrate crystallising in the form $\text{Sm}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$. With K_2SO_4 and Na_2SO_4 , it forms double salts which dissolve with difficulty. The *acid sulphate*, $\text{Sm}_2(\text{SO}_4)_3 \cdot 3\text{H}_2\text{SO}_4$, forms golden-yellow needles. The *nitrate* has the composition $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$. Clève obtained a whole series of other salts of samarium; for instance, $2\text{SmCl}_3 \cdot 2\text{PtCl}_4 \cdot 21\text{H}_2\text{O}$, $\text{Sm}[\text{Pt}_3(\text{CN})_9] \cdot 18\text{H}_2\text{O}$, forming yellow prisms with a blue lustre, &c. The *carbide*, SmC_2 , forms transparent yellow hexagonal crystals which are decomposed by water, with the evolution of hydrocarbons rich in acetylene. The oxide of samarium is a weaker base than Nd_2O_3 .

Europium, $\text{Eu} = 151$ (about).—The salts of this element were obtained by Demarçay from the former samarium by crystallising the nitrates from a concentrated nitric acid solution, and also from the double salts $2\text{R}(\text{NO}_3)_3 \cdot 3\text{Mg}(\text{NO}_3)_2 \cdot 24\text{H}_2\text{O}$; its atomic weight and the spectrum of its chloride form the most characteristic properties of europium. The existence of this element was already suspected by Crookes and Lecoq de Boisbaudran.

Gadolinium, $Gd = 156.4$, was discovered by Marignac in 1880 as *Ya*. The solubility of its nitrate in concentrated nitric acid gives the best means, with other fractional methods, of separating this element. Gadolinium only forms one oxide, Gd_2O_3 , which is a white powder, readily soluble in acids, having the sp. gr. 7.41 and the volume 49. The salts of the type GdX_3 are colourless and do not give any absorption spectrum. Benedicks investigated $GdCl_3 \cdot 6H_2O$, forming crystals of the cubic system, $GdBr_3 \cdot 6H_2O$ and $Gd(NO_3)_3$ with 5 and $6\frac{1}{2} H_2O$. The double nitrate with NH_4NO_3 occurs in deliquescent needles, like those of all the elements of the yttrium group. The *sulphate*, $Gd_2(SO_4)_3 \cdot 8H_2O$, is isomorphous with $Y_2(SO_4)_3 \cdot 8H_2O$, and yields the anhydrous salt, $Gd_2(SO_4)_3$, when heated to 130° . The double sulphate with K_2SO_4 is soluble in a solution of K_2SO_4 . The following salts are also known: $GdCl_3 \cdot PtCl_4 \cdot 10H_2O$, the reddish-green $2Gd(CN)_3 \cdot 3Pt(CN)_2 \cdot 18H_2O$, and the *oxalate* $Gd_2(C_2O_4)_3 \cdot 10H_2O$.

Terbium, $Tb = 148-159-163$?—According to the researches of Mozander, Delafontaine, Marignac, Roseoe, Lecoq de Boisbaudran, Clève, and others, an earth exists which, when obtained by gently igniting the oxalate, turns dark-orange owing to the presence of the higher oxide, but which loses this coloration and turns white when reduced by hydrogen. It forms colourless salts which have no absorption spectrum. The sulphate, $Tb_2(SO_4)_3 \cdot 8H_2O$, is isomorphous with the yttrium salt. The *double sulphate* with K_2SO_4 stands, as regards its solubility, between those of the cerite and yttrium earths, as also is the case with the formate. In fractionating the terbium earths Lecoq found that they give a characteristic rotation spectrum, and Roseoe and Schuster investigated and measured the spark spectrum of the chloride. But Hoffmann and Krüss, notwithstanding the most careful fractional subdivision, could not obtain an earth with a constant molecular weight.

Erbium, *Er*, **Holmium**, *Ho*, **Thulium**, *Tu*, **Dysprosium**, *Dy*.—None of the compounds of these elements have been obtained in a state of purity, and it is only known that their atomic weights lie approximately between 160 and 170. It has already been mentioned that Marignac separated ytterbium, giving colourless salts from the former oxide of erbium, obtained by Bar and Bunsen. The name of erbium was then left to denote the yttrium earth, which gives rose-coloured salts and a bright spectrum and a characteristic absorption spectrum. Clève showed in 1880 that true erbium is accompanied by two other earths, holmium and thulium, which are difficult to separate. Oxide of holmium or the element X which Soret had previously discovered, more closely resembles the yttrium earth, while thulium approaches nearer to oxide of ytterbium. Lecoq de Boisbaudran showed that still another oxide may be separated from oxide of holmium, namely, oxide of dysprosium, and Crookes finds that this is also a complex body. According to Clève the atomic weight of erbium is 166.3, that of holmium less than 165, and that of thulium, *Tu*, about 170.7. The researches of Hoffmann and Krüss (1893), who subjected mixtures of these earths to a thorough fractional separation, showed that the products obtained by the methods then in vogue contain elements with an atomic weight of approximately $R = 166$, and that the distinct spectra of erbium and holmium show that these earths *may be further split up into several very similar earths* by a method of fractional analysis. Of

the compounds of the mixture known as erbium, the oxide, Er_2O_3 , is rose-coloured, and has the sp. gr. 8.64; the sulphate, $\text{Er}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$, forms rose-coloured monoclinic crystals isomorphous with those of the salt of yttrium. It gives a very soluble double salt with K_2SO_4 . Besides these, $\text{Er}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and $\text{Er}_2[\text{Pt}(\text{CN})_4]_3 \cdot 12\text{H}_2\text{O}$, which forms red prisms with a lilac and green lustre, are also known. A hydrate of the peroxide, Er_2O_5 , is obtained by the action of peroxide of hydrogen and alkalies.

Ytterbium. $\text{Yb} = 173$ (Nilson and A. Clève).—The oxide of the former ytterbium discovered by Marignac in 1878 was split up by Nilson (1880) into the weaker basic oxide of scandium and the more energetic basic oxide of pure ytterbium. This is the weakest base of all the yttrium earths. The only known oxide, Yb_2O_3 , is a white powder which dissolves slowly in cold acids and has the sp. gr. 9.18. The salts of ytterbium are colourless and have no absorption spectrum; alkalies precipitate a colourless hydroxide from their solutions. Aqueous solutions of ytterbia in hydrochloric acid give $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$ when evaporated. When heated in a stream of HCl gas it gives YbOCl and not YbCl_3 , like the more energetic basic earths of this group. $\text{Yb}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ is comparatively soluble in cold water and crystallises in large transparent prisms like the salt of yttrium. More dilute solutions are partially decomposed by water, like a salt of a weak base. $\text{Yb}(\text{NO}_3)_3$ crystallises with 3 and 4 H_2O . Nilson and Clève (1902) described many other neutral and basic salts, such as the carbonate, phosphate, &c. The oxalate, $\text{Yb}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$, dissolves with greater ease than any of the analogous salts of the rare metals in a solution of ammonium oxalate and in dilute sulphuric acid. The spark spectrum is very rich in lines (Thalén).

As has already been stated, some chemists, and especially Crookes, Lecoq de Boisbaudran, and Demarçay, conclude from the spectra that there exist several other elements of the rare earths. The independent existence of the *decipium* of Delafontaine and the *victorium* of Crookes is, however, most doubtful. I consider the latter to be a mixture composed chiefly of yttrium and terbium, as there is no place for an element with an atomic weight $R = 117$ in the periodic system.

As regards the position of the group of rare earth elements which begins with $\text{Ce} = 140$ and ends with $\text{Yb} = 173$ in the periodic system, these elements and also cerium are difficult to arrange in this system in its present form. Brauner (*Journal of the Russian Physico-Chemical Society*, 1902, xxxiv. pp. 142–153) makes the proposition that, just as in the eighth group, four elements occupy one place in the system, so also the elements of the rare earths form a node or bands and occupy the position IV., 8 which was formerly occupied by cerium alone. Brauner therefore proposes to pass directly in the 8th series of the periodic system from Ce, &c., to Ta, and to give it the following form:—

Groups :	0	I	II	III	IV	V	VI	VII	VIII
Series 8	Xe 128	Cs 133	Ba 137	La 139	Ce &c. 140–178	Ta 182	W 184	190	Os 191 Ir 193 Pt 1
Where :	Ce &c. = Ce	Pr	Nd	Sm	Eu	Gd	Tb	Ho	Er Tu Yb
„	140–178 = 140	141	144	148	151	156	163 ?	165 ?	166 ? 171 ? 173

The uses of the rare earths in the arts are very limited. The dioxide of cerium is added to the oxide of thorium (1 per cent. of CeO_2 to 99 of ThO_2) in order to render it more luminous for use in Welsbach burners. Besides this, CeO_2 is employed for staining glass yellow and for fining black aniline dye. The oxalate of the higher oxide of cerium is also being used in medicine. Didymium is employed for clearing glasses; and, lastly, the crude mixture of the cerite earths (obtained from monazite as a by-product in the preparation of nitrate of thorium) is used for making fusible glasses and in the manufacture of china.

B. BRAUNER.

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CHAPTER XVIII

SILICON AND THE OTHER ELEMENTS OF THE FOURTH GROUP

CARBON, which gives the compounds CH_4 and CO_2 , belongs to the fourth group of elements. The nearest element to carbon is silicon, which forms the compounds SiH_4 and SiO_2 ; its relation to carbon is like that of aluminium to boron or that of phosphorus to nitrogen. As carbon composes the principal and most essential part of animal and vegetable substances, so is silicon almost an invariable component of the rocky formations of the earth's crust. Silicon hydride, SiH_4 , like CH_4 , has no acid properties, but silica, SiO_2 , resembles carbonic anhydride in possessing feeble acid properties. In a free state silicon is as non-volatile and non-energetic a non-metal as carbon. The form and nature of the compounds of carbon and silicon are therefore very similar. In addition to this resemblance, silicon presents one exceedingly important distinction from carbon, its higher oxygen compound, namely, **silica**, silicon dioxide, or silicic anhydride, SiO_2 being a solid, non-volatile, and exceedingly infusible substance, very unlike carbonic anhydride, CO_2 , which is a gas. This expresses the essential peculiarity of silicon. The cause of this distinction may be most probably sought for in the polymeric nature of the composition of silica as compared with that of carbonic anhydride. The molecule of carbonic anhydride has the composition CO_2 , as is seen by the density of the gas. The molecular weight and vapour density of silica, were it volatile, would probably correspond with the formula SiO_2 ; but it might be imagined that it would correspond to a far higher molecular weight, Si_nO_{2n} , principally from the fact that SiH_4 is a gas like CH_4 , and SiCl_4 is liquid and volatile, boiling at 57° —that is, even lower than CCl_4 , which boils at 76° . In general, analogous compounds of silicon and carbon have nearly the same boiling-points if they are liquid and volatile.¹

¹ Chloroform, CHCl_3 , boils at 60° , and silicon chloroform, SiHCl_3 , at 34° ; silicon ethyl, $\text{Si}(\text{C}_2\text{H}_5)_4$, boils at about 150° , and its corresponding carbon compound, $\text{C}(\text{C}_2\text{H}_5)_4$, at about 120° ; ethyl orthosilicate, $\text{Si}(\text{OC}_2\text{H}_5)_4$, boils at 160° , and ethyl orthocarbonate, $\text{C}(\text{OC}_2\text{H}_5)_4$, at 158° . The specific volumes in a liquid state—that is, those of the silicon compounds—are generally slightly greater than those of the carbon compounds; for example, the volumes of $\text{CCl}_4=94$, $\text{SiCl}_4=112$, $\text{CHCl}_3=81$, $\text{SiHCl}_3=82$, of $\text{C}(\text{OC}_2\text{H}_5)_4$

From this it might be expected that silicic anhydride, SiO_2 , would be a gas like carbonic anhydride, whilst in reality silica is a hard non-volatile substance,^{1a} so that it may with great certainty be considered that in this condition it is polymeric with SiO_2 , as on polymerisation—for instance, when cyanogen passes into paracyanogen, or hydrocyanic acid into cyanuric acid (Chap. IX.)—very frequently gaseous or volatile substances change into solid, non-volatile, and physically denser and more complex substances.² We shall first make acquaintance with free silicon and its volatile compounds, as substances in which the analogy of silicon with carbon is shown, not only in a chemical, but also in a physical sense.³

=186, and $\text{Si}(\text{OC}_2\text{H}_5)_4=201$. The corresponding salts have also nearly equal specific volumes—for example, that of CaCO_3 is 37, and that of $\text{CaSiO}_3=41$. It is impossible to compare SiO_2 and CO_2 , because their physical states are so widely different.

^{1a} But silica fuses and volatilises (Moissan) in the electric furnace—at about 3000° —and is also partially volatile at the temperature attained in the flame of detonating gas (Cremer, 1892).

² A property of intercombination is observable in the atoms of carbon, and a faculty for intercombination, or polymerisation, is also seen in the unsaturated hydrocarbons and carbon compounds in general. In silicon a property of the same nature is found to be particularly developed in silica, SiO_2 ; but this is not the case with carbonic anhydride. The faculty of the molecules of silica for combining both with other molecules and among themselves is exhibited in the formation of most varied compounds with bases, in the formation of hydrates with a gradually decreasing proportion of water down to anhydrous silica, in the colloid nature of the hydrate (the molecules of colloids are always complex), in the formation of polymeric ethereal salts, and in many other properties which will be considered in the sequel. Having come to this conclusion as to the polymeric state of silica as long ago as 1850–1860, I have found it to be confirmed by all subsequent researches on the compounds of silica, and, if I mistake not, this view has now been very generally accepted.

³ It was only after Gerhardt, and in general subsequently to the establishment of the true atomic weights of the elements (Chap. VII.), that a true idea of the atomic weight of silicon and of the composition of silica was arrived at from the fact that the molecules of SiCl_4 , SiF_4 , $\text{Si}(\text{OC}_2\text{H}_5)_4$, &c., never contain less than 28 parts of silicon.

The question of the composition of silica was long the subject of the most contradictory statements in the history of science. In the eighteenth century Pott, Bergmann, and Scheele distinguished silica from alumina and lime. In the beginning of the last century Smithson for the first time expressed the opinion that silica was an acid, and the minerals of rocks, salts of this acid. Berzelius determined the presence of oxygen in silica, 8 parts of oxygen being united with 7 of silicon. The composition of silica was first expressed as SiO (and for the sake of shortness S only was sometimes written instead). An investigation into the amount of silica present in crystalline minerals showed that the amount of oxygen in the bases bears a very varied proportion to the amount of oxygen in the silica, and that this ratio varies from 2:1 to 1:3. The ratio 1:1 is also met with, but the majority of such minerals are rare. Other more common minerals contain a larger proportion of silica, the ratio between the oxygen of the bases and the oxygen of the silica being equal to 1:2, or thereabouts; such are the augites, labradorites, oligoclase, talc, &c. The higher ratio 1:3 is known for a widely distributed series of natural silicates—for example, the feldspars. Those silicates in which the amount of oxygen in the bases is equal to that in the silica are termed **monosilicates**; their general formula will be $(\text{RO})_2\text{SiO}_2$ or $(\text{R}_2\text{O}_3)_2(\text{SiO}_2)_3$. Those in which the ratio of the oxygen is equal to 1:2 are termed **bisilicates**, and their general formula will be

Free silicon can be obtained in an amorphous or crystalline state. Amorphous silicon is produced, like aluminium, by decomposing sodium silicofluoride by means of sodium: $\text{Na}_2\text{SiF}_6 + 4\text{Na} = 6\text{NaF} + \text{Si}$. By treating the mass thus obtained with water the sodium fluoride may be extracted and the residue will consist of brown, powdery silicon. In order to free it from any silica which might be formed, it is treated with hydrofluoric acid. The powder of amorphous silicon is not lustrous; when heated it easily ignites, but does not completely burn. It fuses when very strongly heated, and has then the appearance of carbon.⁴

ROSiO_2 or $\text{R}_2\text{O}_3(\text{SiO}_2)_3$. Those in which the ratio is 1 : 3 will be **trisilicates**, and their general formula $(\text{RO})_2(\text{SiO}_2)_3$ or $(\text{R}_2\text{O}_3)_2(\text{SiO}_2)_3$.

In these formulæ the now established composition of SiO_2 —that is, that in which the atom of Si = 28—is employed. Berzelius, who made an accurate analysis of the composition of felspar, and recognised it as a trisilicate formed by the union of potassium oxide and alumina with silica, in just the same manner as the alums are formed by sulphuric acid, gave silica the same formula as sulphuric anhydride—that is, SiO_3 . In this case the formula of felspar would be exactly similar to that of the alums—that is, $\text{KAl}(\text{SiO}_3)_2$, like the alums, $\text{KAl}(\text{SO}_4)_2$. If the composition of silica be represented as SiO_{33} , the atom of silicon must be recognised as equal to 42 (if O = 16; or if O = 8, as it was before taken to be, Si = 21).

The former formulæ of silica, $\text{SiO}(\text{Si} = 14)$, and $\text{SiO}_3(\text{Si} = 42)$, were first changed into the present one, $\text{SiO}_2(\text{Si} = 28)$, on the basis of the following arguments:—An excess of silica occurs in nature, and in silicious rocks free silica is generally found side by side with the silicates, and one is therefore led to the conclusion that it has formed acid salts. It would therefore be incorrect to consider the trisilicates as normal salts of silica, for they contain the largest proportion of silica; it is much better to admit another formula with a smaller proportion of oxygen for silica, and it then appears that the majority of minerals are normal or slightly basic salts, while some of the minerals abounding in nature contain an excess of silica—that is, belong to the order of acid salts.

At the present time, when there is a general method (Chap. VII.) for the determination of atomic weights, the volumes of the volatile compounds of silica show that its atomic weight is 28, so that silica is SiO_2 . Thus, for example, the vapour density of silicon chloride with respect to air is, as Dumas showed (1862), 5.94, and hence with respect to hydrogen it is 85.5, and its molecular weight consequently 171 (instead of 170, as indicated by theory). This weight contains 28 parts of silicon and 142 parts of chlorine, and therefore the molecule of silicon chloride is SiCl_4 . As two atoms of chlorine are equivalent to one of oxygen, the composition of silica will be SiO_2 —that is, the same as stannic oxide, SnO_2 , or titanic oxide, TiO_2 , and the like, and also the same as carbonic and sulphurous anhydrides, CO_2 and SO_2 . But silica bears but little physical resemblance to the latter compounds, whilst stannic and titanic oxides resemble silica both physically and chemically. They are non-volatile, crystalline, insoluble, colloidal, also form feeble acids like silica, &c., and they might therefore be expected to form analogous compounds, and be isomorphous with silica, as Marignac (1859) found to be actually the case. He obtained stannofluorides, for example, an easily soluble strontium salt, SrSnF_6 , $2\text{H}_2\text{O}$, corresponding with the already long known silicofluorides, MSiF_6 , such as SrSiF_6 , $2\text{H}_2\text{O}$. These two salts are almost identical in crystalline form (monoclinic; angle of the prism, 83° for the former and 84° for the latter; inclination of the axes, $103^\circ 46'$ for the latter and $103^\circ 30'$ for the former), that is, they are isomorphous. We may here add that the specific volume of silica in a solid form is 22.6, and that of stannic oxide 21.5.

⁴ A similar form of silicon is obtained by fusing SiO_2 with magnesium, when an alloy of Si and Mg is also formed (Gattermann). By heating magnesium in a stream of SiF_4 ,

Crystalline silicon is obtained in a similar way, but by substituting an excess of aluminium for the sodium: $3\text{Na}_2\text{SiF}_6 + 4\text{Al} = 6\text{NaF} + 4\text{AlF}_3 + 3\text{Si}$. The part of the aluminium remaining in the metallic state dissolves the silicon, and the latter separates on cooling in a crystalline form. The excess of aluminium is removed after the fusion by means of hydrochloric and hydrofluoric acids. Silica, SiO_2 , is readily reduced by calcium carbide, CaC_2 , in the electric furnace, silicon being formed as a molten mass. Silicon is also reduced at the high temperature of the blast furnace and enters into the composition of the pig iron owing to its ability to form alloys with iron like cast iron. The best silicon crystals are obtained from molten zinc; 15 parts of sodium silicofluoride are mixed with 20 parts of zinc and 4 parts of sodium, and the mixture is thrown into a strongly heated crucible, a layer of common salt being used to cover it; when the mass fuses it is stirred, cooled, treated with hydrochloric acid, and then washed with nitric acid. Like graphite and charcoal, silicon, especially when crystalline, does not in any way act on the above-mentioned acids. It forms black, very brilliant, regular octahedra having a specific gravity of 2.49; it is a bad conductor of electricity, and does not burn even in pure oxygen (but it does in gaseous fluorine). The only acid which acts on it is a mixture of hydrofluoric and nitric acids; but caustic alkalies dissolve in it like aluminium, with evolution of hydrogen, thus showing its acid character. In general, silicon strongly resists the action of reagents, as also do boron and carbon. Crystalline silicon was obtained in 1855 by Deville, and amorphous silicon in 1826 by Berzelius.^{4a}

Silicon hydride, SiH_4 , analogous to marsh gas, was obtained first of all in an impure state, mixed with hydrogen, by two methods: by the action of an alloy of silicon and magnesium on hydrochloric acid,⁵ and

Warren (1888) obtained silicon and its alloy with magnesium. Winkler (1890) found that Mg_3Si_2 and Mg_2Si are formed when SiO_2 and Mg are heated together at lower temperatures, whilst at a high temperature Si only is formed.

^{4a} It is very remarkable that silicon decomposes carbonic anhydride at a white heat, forming a white mass which, after being treated with potassium hydroxide and hydrofluoric acid, leaves a very stable yellow substance of the formula SiCO , which is formed according to the equation, $3\text{Si} + 2\text{CO}_2 = \text{SiO}_2 + 2\text{SiCO}$. It is also slowly formed when silicon is heated with carbonic oxide. It is not oxidised when heated in oxygen. A mixture of silicon and carbon when heated in nitrogen gives the compound $\text{Si}_3\text{C}_2\text{N}$, which is also very stable. On this basis Schützenberger recognises a group, C_2Si_2 , which, like C, is capable of combining with O_2 and N, like C.

We may add that Troost and Hauteffeuille, by heating amorphous silicon in the vapour of SiCl_4 , obtained crystalline silicon, and probably at the same time lower compounds of Si and Cl were temporarily formed. In the vapour of TiCl_4 under the same conditions crystalline titanium is formed (Levy, 1892). Carbon is set free when fused potassium carbonate is heated with silica.

⁵ This alloy, as Beketoff and Chirikoff showed, is easily obtained by directly heating finely divided silica (the experiment may be conducted in a test tube) with magnesium

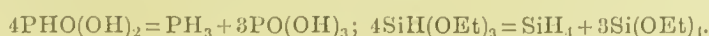
by the action of the galvanic current on dilute sulphuric acid, using electrodes of aluminium containing silicon. In these cases silicon hydride is set free, together with hydrogen, and the presence of the hydride is shown by the fact that the hydrogen separated ignites spontaneously on coming into contact with the air, water and silica being formed. The formation of silicon hydride by the action of hydrochloric acid on magnesium silicide is perfectly akin to the formation of phosphoretted hydrogen by the action of hydrochloric acid on calcium phosphide, to the formation of hydrogen sulphide by the action of acids on many metallic sulphides, and to the formation of hydrocarbons by the action of hydrochloric acid on white cast iron. On heating silicon hydride—that is, on passing it through an incandescent tube—it is decomposed into silicon and hydrogen, just like the hydrocarbons; but the caustic alkalies, although without action on the latter, react with silicon hydride according to the equation: $\text{SiH}_4 + 2\text{KHO} + \text{H}_2\text{O} = \text{SiK}_2\text{O}_3 + 4\text{H}_2$.

Silicon chloride, SiCl_4 , is obtained from amorphous anhydrous

powder (Chap. XIV., notes 17 and 18). The substance formed, when thrown into a solution of hydrochloric acid, evolves spontaneously inflammable and impure silicon hydride, so that the self-inflammability of the gas is easily demonstrated by this means.

In 1850–60 Wöhler and Buff obtained an alloy of silicon and magnesium by the action of sodium on a molten mixture of magnesium chloride, sodium silicofluoride, and sodium chloride. The sodium then simultaneously reduces the silicon and magnesium.

Friedel and Ladenburg subsequently prepared silicon hydride in a pure state, and showed that it is not spontaneously inflammable in air, at the ordinary pressure, but that, like PH_3 , and like the mixture prepared by the above methods, it easily takes fire in air under a lower pressure or when mixed with hydrogen. They prepared the pure compound in the following manner: Wöhler showed that when dry hydrochloric acid gas is passed through a slightly heated tube containing silicon it forms a very volatile colourless liquid, which fumes strongly in air: this is a mixture of silicon chloride, SiCl_4 , and **silicon chloroform**, SiHCl_3 , which corresponds with ordinary chloroform, CHCl_3 . This mixture is easily separated by distillation, because silicon chloride boils at 57° , and silicon chloroform at 36° . The formation of the latter will be understood from the equation, $\text{Si} + 3\text{HCl} = \text{H}_2 + \text{SiHCl}_3$. It is a colourless inflammable liquid of specific gravity 1.6. It forms a transition product between SiH_4 and SiCl_4 , and may be obtained from silicon hydride by the action of chlorine and SbCl_5 , and is itself also transformed into silicon chloride by the action of chlorine. Gattermann obtained SiHCl_3 by heating the mass obtained after the action (note 4) of Mg upon SiO_2 , in a stream of chlorine (with HCl) at about 470° . Friedel and Ladenburg, by acting on anhydrous alcohol with silicon chloroform, obtained an ethereal compound having the composition $\text{SiH}(\text{OC}_2\text{H}_5)_3$. This ether boils at 136° , and when acted on by sodium disengages silicon hydride, and is converted into ethyl orthosilicate, $\text{Si}(\text{OC}_2\text{H}_5)_4$, according to the equation: $4\text{SiH}(\text{OC}_2\text{H}_5)_3 = \text{SiH}_4 + 3\text{Si}(\text{OC}_2\text{H}_5)_4$ (the sodium seems to be unchanged), which is exactly similar to the decomposition of the lower oxides of phosphorus, with the evolution of phosphoretted hydrogen. If we designate the group C_2H_5 contained in the silicon ethers by Et, the parallel is found to be exact:



silica (made by igniting the hydrate) mixed with charcoal,⁶ heated to a white heat in a stream of dry chlorine—that is, by that general method by which many other chloranhydrides having acid properties are obtained. It is also formed by heating silicon in a stream of dry chlorine gas. Silicon chloride is purified from free chlorine by distillation over metallic mercury. Free silicon forms the same substance when treated with dry chlorine. It is a volatile colourless liquid, which boils at 59° and has a specific gravity of 1.52. It fumes strongly in air, has a pungent smell, and in general has the characteristic properties of the acid chloranhydrides. It is completely decomposed by water, forming hydrochloric acid and silicic acid, according to the equation: $\text{SiCl}_4 + 4\text{H}_2\text{O} = \text{Si}(\text{OH})_4 + 4\text{HCl}$.⁷

⁶ The amorphous silica is mixed with starch, dried, and then charred by heating the mixture in a closed crucible. A very intimate mixture of silica and charcoal is thus formed. In Chapter XI., note 13, we saw that elements like silicon disengage more heat with oxygen than with chlorine, and therefore their oxygen compounds cannot be directly decomposed by chlorine, but that this can be effected when the affinity of carbon for oxygen is utilised to aid the action. When the mass obtained by the action of Mg upon SiO_2 is heated to 300° in a current of chlorine, it readily yields SiCl_4 (Gattermann): besides which, two other compounds, corresponding to SiCl_4 , are formed, namely: Si_2Cl_6 , which boils at 145° and solidifies at -1°, and Si_3Cl_8 , which boils at about 212°. Those substances, which answer to corresponding carbon compounds (C_2H_6 and C_3H_8), act upon water and form corresponding oxygen compounds; for instance, $\text{Si}_2\text{Cl}_6 + 4\text{H}_2\text{O} = (\text{SiO}_2\text{H})_2 + 6\text{HCl}$ gives the analogue of oxalic acid (CO_2H)₂. This substance is insoluble in water, decomposes under the action of friction and heat with an explosion, and should be called **silico-oxalic acid**, $\text{Si}_2\text{H}_2\text{O}_4$ (see note 11a).

⁷ Silicon chloride shows a similar behaviour with alcohol. This is accompanied by a very characteristic phenomenon; on pouring silicon chloride into anhydrous alcohol a momentary evolution of heat is observed, owing to a reaction of double decomposition, but this is immediately followed by a powerful cooling effect, due to the disengagement of a large amount of hydrochloric acid—that is, there is an absorption of heat from the formation of gaseous hydrochloric acid. This is a very instructive example in this respect; here two processes, occurring simultaneously—one chemical and the other physical—are divided from each other by time, the latter process showing itself by a distinct fall in temperature. In the majority of cases the two processes proceed simultaneously, and we only observe the difference between the heat developed and absorbed. In acting on alcohol, silicon chloride forms **ethyl orthosilicate**, $\text{SiCl}_4 + 4\text{HOC}_2\text{H}_5 = 4\text{HCl} + \text{Si}(\text{OC}_2\text{H}_5)_4$. This substance boils at 160°, and has a specific gravity 0.94. Another salt, **ethyl metasilicate**, $\text{SiO}(\text{OC}_2\text{H}_5)_2$, is also formed by the action of silicon chloride on anhydrous alcohol: it volatilises above 300°, having a sp. gr. 1.08. It is exceedingly interesting that these two ethereal salts are both volatile, and both correspond with silica, SiO_2 : the first ether corresponds to the hydrate $\text{Si}(\text{OH})_4$, orthosilicic acid, and the second to the hydrate $\text{SiO}(\text{OH})_2$, metasilicic acid. As the nature of hydrates may be judged from the composition of salts, so also, with equal right, can ethereal salts serve the same purpose. The composition of an ethereal salt corresponds with that of an acid in which the hydrogen is replaced by a hydrocarbon radicle—for instance, by C_2H_5 . And, therefore, it may be truly said that there exist at least the two silicic acids above mentioned. We shall afterwards see that there are really several such hydrates; that these ethereal salts actually correspond with hydrates of silica is clearly shown from the fact that they are decomposed by water, and that in moist air they give alcohol and the corresponding hydrate, although the hydrate which is obtained in the

The most remarkable of the haloid compounds of silicon is **silicon fluoride**, SiF_4 . It is a gaseous substance only liquefied by intense cold, -100° , and is obtained (Chap. XI.) directly by the action of hydrofluoric acid on silica and its compounds ($\text{SiO}_2 + 4\text{HF} = 2\text{H}_2\text{O} + \text{SiF}_4$), and also by heating fluor spar with silica ($2\text{CaF}_2 + 3\text{SiO}_2 = 2\text{CaSiO}_3 + \text{SiF}_4$).⁸ In order to prepare silicon fluoride, sand or broken glass is mixed with an equal quantity by weight of fluor spar and 6 parts by weight of strong sulphuric acid, and the mixture gently heated. It fumes strongly in air, reacting with the aqueous vapours, although it is produced from silica and hydrofluoric acid with the separation of water. It is evident that a reverse reaction occurs here; that is to say, the water reacts with the silicon fluoride, but the reaction is not complete. This phenomenon is similar to that which occurs when water decomposes aluminium chloride, but at the same time hydrochloric acid dissolves aluminium hydroxide and forms the same aluminium chloride. The relative amount of water present (together with the temperature) determines the limit and direction of the reaction. The faculty which silicon fluoride has of reacting with water is so great that it takes up the elements of water from many substances—for instance, like sulphuric acid, it chars paper. Water dissolves about 300 volumes of this gas, but in this case it is not a common dissolution which takes place, but a reaction. During the first absorption of silicon fluoride by water, silicic acid is separated in the form of a jelly, but a certain quantity of the silicon fluoride also remains in the liquid, because the hydrofluoric acid

residue always corresponds with the second ethereal salt only—that is, it has the composition $\text{SiO}(\text{OH})_2$; this form corresponds also to carbonic acid in its ordinary salts. This hydrate is formed as a vitreous mass when the ethyl silicates are exposed to air, owing to the action of the atmospheric moisture on them. Its specific gravity is 1.77.

Silicon bromide, SiBr_4 , and **silicon bromoform**, SiHBr_3 , are substances closely resembling the chlorine compounds in their reactions, and they are obtained in the same manner. **Silicon iodoform**, SiHI_3 , boils at about 220° , has a specific gravity of 3.4, reacts in the same manner as silicon chloroform, and is formed, together with silicon iodide, SiI_4 , by the action of a mixture of hydrogen and hydriodic acid on heated silicon. **Silicon iodide** is a solid at the ordinary temperature, fusing at about 120° ; it may be distilled in a stream of carbonic anhydride, but readily takes fire in air, and behaves with water and other reagents just like silicon chloride. It may be obtained by the direct action of the vapour of iodine on heated silicon. Besson (1891) also obtained SiCl_3I (boils at 113°), SiCl_2I_2 (172°), and SiClI_3 (220°), and the corresponding bromine compounds. All the halogen compounds of Si are capable of absorbing 6 or more NH_3 . Besides which Besson obtained SiSCl_2 by heating Si in the vapour of chloride of sulphur; this compound melts at 74° , boils at 185° , and gives with water the hydrate of SiO_2 , HCl , and H_2S .

* This property of calcium fluoride of converting silica into a gas and a vitreous fusible slag of calcium silicate is frequently taken advantage of in the laboratory and in practice in order to remove silica. The same reaction is employed for preparing silicon fluoride on a large scale in the manufacture of hydrofluosilicic acid (see sequel).

formed dissolves the other part of the silica⁹ and forms the so-called **hydrofluosilicic acid**: $\text{H}_2\text{SiF}_6 = \text{SiF}_4 + 2\text{HF} = \text{SiH}_2\text{O}_3 + 6\text{HF} - 3\text{H}_2\text{O}$, that is to say, a metasilicic acid, SiH_2O_3 , in which O_3 is replaced by F_6 . This view of the composition of hydrofluosilicic acid may be admitted, because it forms a whole series of crystallisable and well-defined salts. In general, the whole reaction of water on silicon fluoride may be expressed by the equation: $3\text{SiF}_4 + 3\text{H}_2\text{O} = \text{SiO}(\text{OH})_2 + 2\text{SiH}_2\text{F}_6$. Hydrofluosilicic acid and silicic acid resemble each other as much, and differ as much, in their chemical character as water and hydrofluoric acid. For this reason silicic acid is a feebler acid than hydrofluosilicic acid, and in addition to this the former is insoluble, and the latter soluble, in water.¹⁰ Hydrofluosilicic acid is also formed when silicic acid is dissolved in a solution of hydrofluoric acid. It is incapable of volatilising without decomposition, and on heating the concentrated acid, silicon fluoride is evolved, leaving an aqueous solution of hydrofluoric acid. This is the reason why solutions of hydrofluosilicic acid corrode glass. This decomposition may be further accelerated by the

⁹ The amount of heat developed by the solution of silicic acid, $\text{SiO}_2, n\text{H}_2\text{O}$, in aqueous hydrofluoric acid, $x\text{HF}, n\text{H}_2\text{O}$, increases with the magnitude of x and normally equals $x5600$ heat units, where x varies between 1 and 8. However, when $x=10$, the maximum amount of heat is developed ($=49,500$ units), and beyond that the amount decreases (Thomsen).

¹⁰ In reality, however, it would seem that the reaction is still more complex, because the aqueous solution of silicon fluoride does not yield a hydrate of silica, but a fluo-hydrate (Schiff), $\text{Si}_2\text{O}_3(\text{OH})\text{F}$, corresponding to the (pyro-) hydrate $\text{Si}_2\text{O}_3(\text{OH})_2$, equal to $\text{SiO}(\text{OH})_2, \text{SiO}_2$, so that the reaction of silicon fluoride on water is expressed by the equation: $5\text{SiF}_4 + 4\text{H}_2\text{O} = 3\text{SiH}_2\text{F}_6 + \text{Si}_2\text{O}_3(\text{OH})\text{F} + \text{HF}$. However, Berzelius states that the hydrate, when well washed with water, contains no fluorine, which is probably due to the fact that an excess of water decomposes $\text{Si}_2\text{O}_3(\text{OH})\text{F}$, forming hydrofluoric acid and the 'compound' $\text{Si}_2\text{O}_3(\text{OH})_2$. Water saturated with silicon fluoride disengages silicon fluoride and hydrofluoric acid when treated with hydrochloric acid, the gelatinous precipitate being simultaneously dissolved. It may be further remarked that hydrofluosilicic acid has been frequently regarded as $\text{SiO}_2, 6\text{HF}$, because it is formed by the solution of silica in hydrofluoric acid, but only two of these six hydrogens are replaced by metals. On concentration, solutions of the acid begin to decompose when they reach a strength of $6\text{H}_2\text{O}$ per H_2SiF_6 , and therefore the acid may be regarded as $\text{Si}(\text{OH})_4, 2\text{H}_2\text{O}, 6\text{HF}$, but the corresponding salts contain less water, and there are even anhydrous salts, R_2SiF_6 , so that the acid itself is most simply represented as H_2SiF_6 .

If gaseous silicon fluoride be passed directly into water, the gas-conducting tube becomes clogged with the precipitated silicic acid. This is best prevented by immersing the end of the tube under mercury, and then pouring water over the mercury; the silicon fluoride then passes through the mercury, and only comes into contact with the water at its surface, and consequently the gas-conducting tube remains unobstructed. The silicic acid thus obtained soon settles, and a colourless solution with a pleasant but distinctly acid taste is procured.

Mackintosh, by taking 9 per cent. of hydrofluoric acid, observed that in the course of an hour its action on opal attained 77 per cent. of the possible amount, whilst the action on quartz during the same time did not exceed $1\frac{1}{2}$ per cent. of its possible value. This shows the difference in structure of these two modifications of silica, which will be more fully described in the sequel.

addition of sulphuric acid, or even of other acids. Hydrofluosilicic acid, when acting on potassium and barium salts, gives precipitates, because the salts of these metals are but sparingly soluble in water: thus, $2\text{KX} + \text{H}_2\text{SiF}_6 = 2\text{HX} + \text{K}_2\text{SiF}_6$. The potassium salt is obtained in the form of very fine octahedra, but the precipitate does not form quickly, and at first appears as a jelly. Nevertheless, the decomposition is complete, and is taken advantage of for obtaining from salts of potassium their corresponding acids.^{10a}

Silicon, having so much in common with carbon, is also able to combine with it in the proportion given by the law of substitution, that is, it forms a **carbide of silicon**, CSi , called **carborundum** and obtained by Mühlhäuser and Aitchison in the United States, and by Moissan in France (1891), and others, by reducing silica with carbon in the electric furnace at a temperature of about $2,500^\circ$,¹¹ i.e., by the action of an electric current upon a mixture of carbon and SiO_2 with NaCl . After treating the resultant mass with acids and washing with water, carborundum is obtained in transparent, lustrous grains of a greenish colour, possessing great hardness (greater than that of corundum) and therefore used for polishing the hardest kinds of steel and stones. The specific gravity is about 3.1. Carborundum does not alter at a red heat, does not burn, and apparently approaches the diamond in its properties. (In 1894 Moissan obtained a similar very hard compound for boron, B_6C , sp. gr. 2.5.)

According to the principle of substitution, if silicon forms SiH_4 , a series of hydrates, or hydroxyl derivatives, ought to exist corresponding with this hydride. The first hydrate of an alcoholic character ought to have the composition $\text{SiH}_3(\text{OH})$; the second hydrate, $\text{SiH}_2(\text{OH})_2$; the third, $\text{SiH}(\text{OH})_3$; ^{11a} and the last, $\text{Si}(\text{OH})_4$. The last is a hydrate of

^{10a} The sodium salt is far more soluble in water, and crystallises in the hexagonal system. The magnesium salt, MgSiF_6 , and calcium salt are soluble in water. The salts of hydrofluosilicic acid may be obtained not only by the action of the acid on bases or by double decompositions, but also by the action of hydrofluoric acid on metallic silicates. Sulphuric acid decomposes them, with evolution of hydrofluoric acid and silicon fluoride, and the salts when heated evolve silicon fluoride, leaving a residue of metallic fluoride, R_2F_2 .

¹¹ See note 4a. Probably, in his researches, Schützenberger had already obtained CSi together with other silicon compounds. An amorphous, less hard compound of the same alloy is also obtained together with the hard crystalline CSi .

^{11a} The following consideration is very important in explaining the nature of the lower hydrates which are known for silicon. If we suppose water to be taken up from the first hydrates (just as formic acid is $\text{CH}(\text{OH})_3$, *minus* water), we shall obtain the various lower hydrates corresponding with silicon hydride. When ignited they should, like phosphorous and hypophosphorous acids, disengage silicon hydride, and behind leave a residue of silica—i.e., of the oxide corresponding to the highest hydrate—just as organic hydrates (for example, formic acid with an alkali) form carbonic anhydride as the highest oxygen compound. Such imperfect hydrates of silicon, or, more correctly speaking, of

silica, because it is equal to $\text{SiO}_2 + 2\text{H}_2\text{O}$; and it is formed by the action of water on silicon chloride, when all four atoms of chlorine are replaced by four hydroxyl groups.

Silica or silicic anhydride, both in the free state and in combination with other oxides, enters into the composition of most of the rock formations of the earth's crust. These silicious compounds are substances varying so much in their properties, crystalline forms, and relations to one another that they are comprised (like the carbon compounds) in a special branch of natural science, and are treated of in works on mineralogy; so that, in dealing with them further, we shall only give a short description of these various compounds. It is first of all necessary to turn to the description of silica itself, especially as it is not infrequently met with in nature in a separate state, and often forms whole masses of rock formations called 'quartz.' In an anhydrous condition silica appears in the greatest variety of natural forms—sometimes in well-formed crystals, hexagonal prisms, terminated by hexagonal pyramids. If the crystals are colourless and transparent, they are called **rock crystal**. This is the purest form of silica. Prismatic crystals of rock crystal sometimes attain considerable size, and as they are remarkable for their resistance to change, great hardness, and high index of refraction, they are used for ornaments, seals, necklaces, spectacles, optical instruments, &c.¹² Rock crystal coloured with

silicon hydride, were first obtained by Wöhler (1863) and studied by Geuther (1865), (see note 6).

Leucone is a white hydrate of the composition $\text{SiH}(\text{OH})_3$. It is obtained by slowly passing the vapour of silicon chloroform into cold water: $\text{SiHCl}_3 + 3\text{H}_2\text{O} = \text{SiH}(\text{OH})_3 + 3\text{HCl}$. But this hydrate, like the corresponding one of phosphorus or carbon, does not remain in this state of hydration, but loses a portion of its water. The carbon hydrate of this nature, $\text{CH}(\text{OH})_3$, loses water and forms formic acid, $\text{CHO}(\text{OH})$; but the silicon hydrate loses a still greater proportion of water, $2\text{SiH}(\text{OH})_3$, parting with $3\text{H}_2\text{O}$, and consequently leaving $\text{Si}_2\text{H}_2\text{O}_3$. This substance must be an anhydride; all the hydrogen previously in the form of hydroxyl has been disengaged, two remaining hydrogens being left from SiH_4 . The other similar hydrate is also white, and has the composition $\text{Si}_3\text{H}_2\text{O}$ (nearly). It may be regarded as the above white hydrate + SiO_2 . A yellow hydrate, known as **chryseone** (silicone), is obtained by the action of hydrochloric acid on an alloy of silicon and calcium: its composition is approximately $\text{Si}_6\text{H}_4\text{O}_3$. Most probably, however, chryseone has a more simple composition, and stands in the same relation to the hydrate $\text{SiH}_2(\text{OH})_3$ as leucone does to the hydrate $\text{SiH}(\text{OH})_3$, because this very simply expresses the transition of the first compound into the second with the loss of water, $\text{SiH}_2(\text{OH})_2 - \text{H}_2 + \text{H}_2\text{O} = \text{SiH}(\text{OH})_3$. When these lower hydrates are ignited without access of air, they are decomposed into hydrogen, silicon, and silica—that is, it may be supposed that they form silicon hydride (which decomposes into silicon and hydrogen) and silica (just as phosphorous and hypophosphorous acids give phosphoric acid and phosphoretted hydrogen). When ignited in air, they burn, forming silica. They are none of them acted on by acids, but when treated with alkalis evolve hydrogen and give silicates; for example, with leucone: $\text{SiH}_2\text{O}_3 + 4\text{KHO} = 2\text{SiK}_2\text{O} + \text{H}_2\text{O} + 2\text{H}_2$. They have no acid properties.

¹² Two modifications of rock crystal are known. These are very easily distinguished

organic matter in contact with which it has been produced has a brown or greyish colour, and then bears the name of **cairngorm** or **smoky quartz**. In this form it has the same uses as rock crystal, especially as it is often found in large masses. The same mineral frequently occurs, especially in aqueous formations, coloured lilac-red or pink by manganese or iron oxides, and is then known as **amethyst**. When finely coloured the amethyst is used as a precious stone, but amethysts most frequently occur as small crystals in the cavities formed in other rocky formations, and especially in those formed in silica itself. A similar anhydrous silica is often found in transparent non-crystalline masses, having the same specific gravity as rock crystal itself (2.66). In this case it is called **quartz**. Sometimes it forms complete rock formations, but more often penetrates or is interspersed through other rock formations, together with other silicious compounds. Thus, in granite, quartz is mixed with felspar and similar substances. Sometimes the colouring of quartz is so considerable that it is hardly transparent even in thin sheets, but it is often found in transparent masses slightly coloured with various tints. The existence in nature of enormous masses of quartz proves that it resists the action of water. When water destroys rock formations, the silicious minerals which they contain are partly dissolved and partly transformed into clay, &c. But the quartz remains untouched, in the form of the grains in which it existed in the rocky formation; sometimes, when crushed, it is carried away by the water and deposited. This is the origin of **sand**. Naturally, sometimes other rocky substances which are not changed by water, or only slightly acted on by it, are found in sand; but as these latter are more or less changed by the continuous action of water, it is not unusual to find sand which consists almost entirely of pure quartz. Common sand is generally coloured yellow or reddish brown by foreign mineral matter, consisting principally of ferruginous minerals and clays. The purest or so-called quartz sand is, however, rarely found, and is recognised by the absence of colour, and also by the test that when shaken in water it does not form any turbidity, which shows the absence of clay; when fused with bases it forms a colourless glass, and on this

from each other by their relation to polarised light: one rotates the plane of polarisation to the right and the other to the left—in the one the hemihedral faces are to the right and in the other to the left. This opposite rotatory power is taken advantage of in the construction of polarisers. But accompanying this physical difference—which is naturally dependent on a certain difference in the distribution of the molecules—there is not only no observable difference in the chemical properties, but none even in the density of the mass. Perfectly pure rock crystal is a substance which is most invariable with respect to its specific gravity. The numerous and accurate determinations made by Steinheil on the specific gravity of rock crystal show that (if the crystal be free from flaws) it is very constant and equal to 2.66.

account is a valuable material for the manufacture of glass. Sands were formed at all periods of the earth's existence; the ancient ones, compressed by strata of more recent formation and permeated with various substances (deposited from the infiltrating water), are sometimes solidified into rock, called **sandstone**, composing, in some places, whole mountain chains, and serviceable as a most excellent building material, on account both of the slight change it undergoes, under the influence of atmospheric agencies and of the facility with which it may be wrought from rock formations into immense regularly shaped flags—the latter property is due to the primary laminar structure of the sand formations deposited, as above mentioned, by water. Many grindstones and whetstones are made from such rocks.

Anhydrous silica, SiO_2 , is known not only in the condition of rock crystal and quartz, having a specific gravity of 2.6, but also in a special form, having other chemical and physical properties. This variety of silica has a specific gravity of 2.2, and is formed by fusing rock crystal or heating silicic acid.^{12a} Silicic acid, when heated to a dull red heat, parts entirely with the water it contains, and leaves an exceedingly fine amorphous mass of silica (easily levigated, but difficult to moisten); it is characterised by such excessive friability that, when lightly blown on, a large mass of it rises into the air like a cloud of dust. A mass of anhydrous silica may be poured in this way from one vessel to another like a liquid, and like the latter it takes a horizontal position in the vessel containing it.¹³ Anhydrous silica, like quartz,^{13a} does not fuse in the heat of a furnace, but it fuses in the oxyhydrogen flame to a colourless glassy mass exactly similar to that formed in the same way from rock crystal. In this condition silica has a specific gravity of 2.2.^{13b}

^{12a} Several other modifications are known as minute crystals. For example, there is a particular mineral first found in Styria and known as **tridymite**. Its specific gravity, 2.3, and the form of its crystals clearly distinguish it from rock crystal; its hardness is the same as that of quartz—that is, below that of the ruby, but greater than that of felspar and glass.

¹³ There is a distinct rise of temperature (about 4°) when amorphous silica is moistened with water. Benzene and amyl alcohol also give an observable rise of temperature. Charcoal and sand give the same result, although to a less extent.

^{13a} Silica fused in the oxyhydrogen flame can be drawn into the finest threads (Boys) which are employed for supporting magnets and in physical apparatus dependent on torsion.

^{13b} Silica also occurs in nature in two modifications. The opal and tripoli (infusorial earth) have a specific gravity of about 2.2, and are comparatively easily soluble in alkalis and hydrofluoric acid. Chalcedony and flint (tinted quartzose concretions of aqueous origin), agate and similar forms of silica of undoubted aqueous origin, although still containing a certain amount of water, have a specific gravity of 2.6, and correspond with quartz in the difficulty with which they dissolve. This form of silica sometimes permeates the cellulose of wood, forming one of the ordinary kinds of petrified wood. The silica may be extracted from it by the action of hydrofluoric acid, and the cellulose remains behind, clearly showing that silica in a soluble form (see sequel) has permeated

Both forms of silica are insoluble in ordinary acids, and even when they are in the state of powder, alkalis in solution act very slowly and feebly on them; rock crystal offers much greater resistance to the action of alkalis than the powder obtained by heating the hydrate. The latter is quite soluble, although but slowly, in hot alkaline solutions. This last property appertains in a greater degree to anhydrous silica having a specific gravity of 2.2 than to that which has a specific gravity of 2.6. Hydrofluoric acid more easily transforms the former into silicon fluoride than it does the latter. Both varieties of silica, when taken in the form of powder, combine readily with bases, forming, on being fused with an alkali, a vitreous slag, which is a salt corresponding with silica. Glass is such a salt, formed of alkalis and alkaline earthy bases; if the glass does not contain any of the latter—that is, if only alkaline glass is taken—a mass soluble in water is obtained. In order to obtain such **soluble glass**, potassium or sodium carbonate, or, better, a mixture of the two (fusion mixture), is fused with fine sand. A still better and further saturation of the alkalis with silica is effected by the action of alkaline solutions on the silicon hydrate met with in nature; for instance, an alkaline solution is often made use of to act on the so-called **tripoli**, or collection of silicious skeletons of the lowest microscopical infusoria, which is sometimes found in considerable layers in the form of a sandy mass. Tripoli is used for polishing, not only on account of the considerable hardness of the silica, but also because the microscopic bodies of the infusoria have a pointed shape, which, however, is not angular, so that they do not scratch metals like sand.¹⁴ The alkaline solutions of silica obtained by boiling tripoli with caustic soda under pressure contain various proportions of silica and alkali.^{14a} In order that it may contain the greatest

into the cells, where it has deposited the hydrate, which has lost water, and given a silica of sp. gr. 2.6. The quartzose stalactites found in certain caves are also evidently of a similar aqueous origin; their sp. gr. is also 2.6. As crystals of amethyst are frequently found among chalcedonies, and as Friedau and Sarrau (1879) obtained crystals of rock crystal by heating soluble glass with an excess of hydrate of silica in a closed vessel, there is no doubt but that rock crystal itself is formed in the wet way from the gelatinous hydrate. Chroustehoff obtained it directly from soluble silica. Thus, this hydrate is able to form not only the variety having the specific gravity 2.2, but also the more stable one of sp. gr. 2.6; and both exist with a small proportion of water and in a perfectly anhydrous state in an amorphous and crystalline form. All these facts are expressed by recognising silica as dimorphous, and their cause must apparently be looked for in a difference in the degree of polymerisation.

¹⁴ Deposits of perfectly white tripoli have been discovered near Batoum, and might prove of some commercial importance; it is sometimes called *kieselguhr*.

^{14a} Alkaline solutions, saturated with silica and known as **soluble glass**, are prepared on a large scale for technical purposes by fusing sand with alkaline carbonates and boiling the resultant glass (crushed) in boilers with water, or by the action of potassium (or sodium) hydroxide in a steam boiler on tripoli or infusorial earth, which contains a large proportion of amorphous silica. All solutions of the alkaline silicates

amount of silica, silicic acid should be added to the heated solution. Silicic acid is formed by taking any solution containing silica and alkali, and adding to it, by degrees, some acid—for instance, sulphuric or hydrochloric. If the experiment be carried on carefully and the solution be concentrated, the whole mass will thicken to a jelly, due to the gelatinous form of the silicic acid separated from the salt by the action of the acid. The decomposition may be expressed by the following equation : $\text{SiNa}_2\text{O}_3 + \text{H}_2\text{O} + 2\text{HCl} = 2\text{NaCl} + \text{Si}(\text{OH})_4$. The hydrate separated, $\text{Si}(\text{OH})_4$, easily loses part of the water and forms a jelly, the whole mass gelatinising if the solution is strong enough.¹⁵

have an alkaline reaction, and are even decomposed by carbonic acid. They are chiefly used by the dyer, for the same purposes as sodium aluminate, and also for giving a hardness and polish to stucco and other cements, and in general to substances which contain lime. A lump of chalk when immersed in soluble glass, or, better still, when moistened with a solution and afterwards washed in water (or, better, in hydrofluosilicic acid, in order to bind together the free alkali and make it insoluble), becomes exceedingly hard, loses its friability, is rendered cohesive, and cannot be levigated in water. This transformation is due to the fact that the hydrate of silica present in the solution acts upon the lime, forming a stony mass of calcium silicate, while the carbonic acid previously in combination with the lime enters into combination with the alkali and is washed away by the water.

¹⁵ The equation given above does not express the actual reaction, for in the first place silica has the faculty of forming compounds with bases, and therefore the formula SiNa_4O_4 is only a particular case, if one may so express oneself. And, in the second place, silica gives several hydrates. In consequence of this, the hydrate precipitated does not actually contain so high a proportion of water as $\text{Si}(\text{OH})_4$, but always less. The insoluble gelatinous hydrate which separates out is able (before, but not after, having been dried) to dissolve in a solution of sodium carbonate. When dried in air its composition corresponds with that of the ordinary salts of carbonic acid—that is, SiH_2O_3 , or $\text{SiO}(\text{OH})_2$. If gradually heated it loses water by degrees, and, in so doing, gives various degrees of combination with it. The existence of these degrees of hydration, having the composition $\text{SiH}_2\text{O}_3, n\text{SiO}_2$, or, in general, $n\text{SiO}_2, m\text{H}_2\text{O}$, where $m < n$, must be recognised, because most varied degrees of combination of silica with bases are known. The hydrate of silica, when not dried above 30° , has a composition of nearly $\text{H}_4\text{Si}_3\text{O}_9 = (\text{H}_2\text{SiO}_3)_2\text{SiO}_2$, but at 60° contains a greater proportion of silica—that is, it loses still more water; and at 100° a hydrate of the composition $\text{SiH}_2\text{O}_3, 2\text{SiO}_2$, and at 250° one having approximately the composition $\text{SiH}_2\text{O}_3, 7\text{SiO}_2$ are obtained.

These data show the complexity of the molecules of anhydrous silica. In the natural hydrates, the decrement of water proceeds quite consecutively, and, so to say, imperceptibly, until n becomes incomparably greater than m , and when the ratio becomes very large, anhydrous silica of the two modifications 2·6 and 2·2 is obtained. Even the composition $(\text{SiO}_2)_{10}, \text{H}_2\text{O}$ corresponds with 2·9 per cent. of water, and natural hydrates often contain still less water than this. Thus some opals are known which contain only 1 per cent. of water, whilst others contain 7 and even 10 per cent. As the artificially prepared gelatinous hydrate of silica when dried has many of the properties of native opals, and as this hydrate always loses water easily and continually, there can be no doubt that the transition of $(\text{SiO}_2)_n(\text{H}_2\text{O})_m$ into anhydrous silica, both amorphous and crystalline, is accomplished gradually. This can only be the case if the magnitude of n be considerable, and therefore the molecule of silica in the hydrate is undoubtedly complex, and hence the anhydrous silica of sp. gr. 2·2 and 2·6 does not contain SiO_2 , but a complex molecule, Si_nO_{2n} —that is, the structure of silica is polymeric and complex, and not simple as represented above by the formula SiO_2 .

Neither of the two varieties of anhydrous silica, nor the various natural gelatinous hydrates, are directly soluble in water. There is, however, a form of silica (or its hydrosol) known as soluble silica. Silica occurs in this state in nature. Small quantities of soluble silica are met with in all waters. Certain mineral springs, and especially hot springs—of which the best known are the Geysers of Iceland and those in the North American National Park (Yellowstone Valley)—contain a considerable amount of silica in solution. Such water, permeating the objects it meets with—for instance, **wood**—penetrates into them and deposits silica inside them, that is, transforms them into a **petrified** condition. Silicious stalactites, and also many (if not all) forms of silica are formed by such water. The absorption of silica by plants by means of their roots, and also by the lower organisms having silicious bodies, is due also to their nourishing themselves with the solutions containing silica which are continually formed in nature. In the straws of the grasses, in hard shave-grass, and especially in the knots of bamboo and other strawlike plants, a considerable quantity of silica is deposited, which must previously have been absorbed by the plants.

Silicic acid is a colloid. The gelatinous silicon hydrate is its hydrogel and the soluble hydrate the hydrosol (Chap. XII.). Both varieties may be easily obtained from the alkaline silicates and from water-glass. The very same substances—that is, aqueous solutions of soluble glass and acid—taken in the same proportion, may produce either the gelatinous or the soluble hydrate of silica, according to the way these solutions are mixed together. If the *acid be added* little by little *to the alkaline silicate*, with continuous stirring, a moment arrives when the whole mass thickens to a jelly—the hydrogel; in this case the silicic acid is formed in the alkaline solution and becomes insoluble. But if the mixing is done in the reverse order—that is, if the soluble glass *is added to the acid*, or if a quantity of acid is rapidly poured into the solution of the salt—then the separation of the silica takes place in the acid liquid, and it is obtained in the form of the soluble hydrate, the hydrosol.¹⁶

The hydrosol of silica prepared by mixing an excess of hydrochloric

¹⁶ The presence of an excess of acid aids the retention of the silica in the solution, because the gelatinous silica obtained in the above manner is more soluble in water containing acid than in pure water. This would seem to indicate a feeble tendency of silica to combine with acids, and it might even have been imagined that in such a solution the hydrate of silica is held in combination by an excess of acid, had Graham not obtained soluble silica perfectly free from acid, and if there were not solutions of silica free from any acid in nature. At all events a tolerably strong solution of free silica or silicic acid may be obtained from soluble glass diluted with water.

acid with a solution of sodium silicate may be freed from the admixtures of both hydrochloric acid and salt, sodium chloride, **by means of dialysis**,¹⁷ as **Graham** showed (in 1861) in inquiring into the nature of colloids (Chap. I.), and making many other important chemical investigations. The solution, containing the acid, salt, and silica, all dissolved in water, is poured into a dialyser—that is, a vessel with a porous diaphragm surrounded by water. Certain substances pass more easily than others through the diaphragm. This may be represented thus: the passage through the diaphragm proceeds in both directions, and if the solutions on each side of the diaphragm be equally strong, there will be equal numbers of molecules of the soluble substance passing into either side in a given time, some passing quickly and others slowly. The metallic chlorides and hydrochloric acid belong to the series of crystalloids which pass easily through a diaphragm, and therefore the hydrochloric acid and sodium chloride contained in the above-mentioned dialyser pass from the solution through the diaphragm into the water of the external vessel with considerable rapidity. The aqueous solution of colloidal silica also penetrates through the diaphragm, but very much more slowly. But if the amount of the dissolved substance is not the same on both sides of the diaphragm, the whole system strives to attain a state of equilibrium; that is, the given substance penetrates through the diaphragm from the side where it is in excess to the part where there is a smaller quantity of it. All substances which are soluble in water have the faculty of penetrating through a membrane swollen in water, but the velocities of penetration are not equal, so that the dialyser separates substances like a sieve. The silica passes less rapidly through the diaphragm than the sodium chloride and hydrochloric acid, so that by repeatedly changing the external water it is easy to effect the extraction of the chlorine compounds from the dialyser, which will finally only contain a solution of silica. This extraction (of HCl and NaCl) may be so complete that the liquid taken from the dialyser will not give any precipitate with a solution of silver nitrate. Graham obtained in this way soluble silica having a distinctly acid reaction, which, however, disappeared on the addition of a very minute quantity of alkali; for ten parts of silica in the solution it was sufficient to take one part of alkali in order to give the liquid an alkaline reaction, so slightly energetic are the acid properties of silicic acid. The solution of silica obtained by this method becomes gelatinous on standing, on being heated, or on evaporation under the

¹⁷ See Chap. I., note 18. A solution of water-glass mixed with an excess of hydrochloric acid is poured into the dialyser, and the outer vessel is filled with water, which is continually renewed. The water carries off the sodium chloride and hydrochloric acid, and the hydrosol remains in the dialyser.

receiver of an air-pump, &c. The hydrosol is transformed into the hydrogel, the soluble hydrate into the gelatinous.

Thus in addition to the gelatinous form of silicic acid, there exists also a variety of this substance, soluble in water, as is the case with alumina. Such variation in properties and exactly the same relations with regard to water characterise an immense series of other substances having a great significance in nature. Such substances are especially numerous among organic compounds, and particularly in those classes which compose the principal material of the bodies of animals and plants. It is sufficient to mention, for instance, the gelatin which is familiar to all as carpenter's and other glues, and in the form of size and jelly. The same substance is also known in the solution which is used to join objects together. In a peculiar insoluble condition it enters into the composition of hides and bones. These various forms of gelatin differ in the same way as the different varieties of silica. The property of forming a jelly is exactly the same as in silica, and the adhesiveness of the solutions of both substances is identical; soluble silica adheres like a solution of gelatin. The same properties are again shown by starch, rosin, albumin, and a number of similar substances. The diaphragms used in dialysis are also insoluble, gelatinous forms of colloids. The bodies of animals and plants consist largely of similar matter, insoluble in water, corresponding with the gelatinous or insoluble silicon hydrate, or with glue. The albumin which coagulates when eggs are boiled is a typical form of the gelatinous condition of such substances in the body. These few indications are sufficient to show how great is the significance of those transformations which are so well marked in silica. The facts, discovered by Graham in 1861-1864, comprise the most essential acquisitions in the general association of these phenomena of nature in the history of organic forms. The facility of transition from hydrogel to hydrosol is the first condition of the possibility of the development of organisms. The blood contains hydrosols, and the hydrogels of the same substances are contained in the muscles and tissues, and especially on the surface, of the body. All tissues are formed from the blood, and in that case the hydrosols are converted into hydrogels.¹⁸ The absence of crystallisation

¹⁸ A similar process occurs in plants. For example, when they secrete a store of material for the following year in their bulbs, roots, &c. (for instance, the potato in its tubers), the solutions from the leaves and stems penetrate the roots and other parts in the form of hydrosols, where they are converted into hydrogels, that is, into an insoluble form, which is acted on with difficulty and is easily kept unaltered until the period of growth—generally the following spring—when they are reconverted into hydrosols, and the insoluble substance re-enters the sap, and serves as a source of the hydrogels in the leaves and other portions of plants.

and the property of passing, apparently under the influence of feeble agencies, from the soluble condition to the insoluble, gelatinous condition, constitute the fundamental properties of all colloids.¹⁹

Silica, by its ability **to form salts**, stands, in the series of oxides, on the boundary line, and occupies, with regard to the acids, just such a place as alumina occupies on the side of the bases—that is, aluminium hydroxide is the representative of the feeblest bases, and silicic acid is the least energetic of acids (at least in the presence of water—that is, in aqueous solutions); in alumina, however, the basic properties are distinctly expressed, whilst in silica the acid properties preponderate. Like all feeble acid oxides it is capable of forming, with other acids, saline compounds which are but slightly stable and are very easily decomposed in the presence of water. The chief peculiarity of the silicates consists in the number of their types. The salts formed with nitric or sulphuric acid exist in one, two, or three tolerably stable forms, but for acids like silicic acid the number of forms is very great—indeed, almost unlimited. The natural silicates in particular furnish proof of this fact; they contain various bases in combination with silica, and for one and the same base there often exist various degrees of combination. As feeble bases are capable of forming basic salts—that is, compounds of a normal salt with a feeble base (either the hydroxide or the oxide)—in addition to normal ones, so the feeble acid oxides (although not all) form, in addition to normal salts, highly acid salts—that is, normal salts *plus* acid (hydrate or anhydride). Such are boric, phosphoric, molybdic, chromic, and especially silicic, acids.

In order to explain these relations it is necessary first to recollect the existence of the various hydrates of silica, or silicic acids,²⁰ and then

¹⁹ As regards their chemical composition the colloids are very complex—that is, they have a high molecular weight and a large molecular volume—in consequence of which they do not penetrate through membranes, and are readily subject to variation in their physical and chemical properties (owing to their complex structure and polymerism?). They have but little chemical energy, and are generally feeble acids, if belonging to the order of oxides or hydrates, such as the hydrates of molybdic and tungstic acids (Chap. XXI.). But now the number of substances capable, like colloids, of passing into aqueous solutions and of easily separating out from them, as well as of appearing in an insoluble form, must be supplemented by various other substances, among which soluble gold and silver (Chap. XXIV.) and other metals are of particular interest. So that now it may be said that the capacity of forming colloid solutions is not limited to a definite class of compounds, but is, if not a general, at all events an exceedingly widely distributed phenomenon. Colloids may be regarded as a kind of transition stage between liquids and solids. Tammann's researches (see Physical Chemistry) on the effect of pressure lead to this conclusion.

²⁰ This is in accordance with the generally accepted representation of the relations between salts and the hydrates of acids, but it is of little help in the study of silicious compounds. Generally speaking, it becomes necessary to explain the power of $(\text{SiO}_2)_n$ to combine with $(\text{RO})_m$, where n may be greater than m , and where R may be

to turn our attention to the similarity between silicon compounds and metallic alloys. Silica is an oxide having the appearance of, and in many respects the same properties as, those oxides which combine with it, and if two metals are capable of forming homogeneous alloys in which there exist definite or indefinite compounds, it is permissible to assume a similar power of forming alloys in the case of analogous oxides. Such alloys are found in indefinite amorphous masses in the form of glass, lava, slags, and a number of similar silicious compounds which do not contain any definite types of combination, but nevertheless are homogeneous throughout their mass. By slow cooling, or under other circumstances, definite crystalline compounds may—and sometimes do—separate from this homogeneous mass, as also sometimes definite crystalline alloys separate from metallic alloys.

The formation of crystalline rocks in nature is partly of such a character. By aqueous or igneous agency, but in any case in a liquid condition, those oxides which form the earth's crust and its crystalline minerals came into mutual contact. First of all they formed a shapeless mass, of which lava, glass, slags, and solutions are examples; and then certain definite compounds of oxides existing in this alloy or in the shapeless mass were formed. This is entirely similar to two metals forming a homogeneous alloy,²¹ and under known circumstances

H_2, Ca , &c. Here we are aided by those facts which have been attained by the investigation of carbon compounds, especially with respect to glycol. Glycol is a compound having the composition $C_2H_6O_2$, only differing from alcohol, C_2H_5O , by an extra atom of oxygen. This hydrate contains two hydroxyl groups, which may be successively replaced by chlorine, &c. Hence the composition of glycol should be represented as $C_2H_4(OH)_2$. It has been found that glycol forms so-called polyglycols. Their origin will be understood from the fact that glycol as a hydrate has a corresponding anhydride of the composition C_2H_4O , known as ethylene oxide. This substance is ethane, C_2H_6 , in which two hydrogens are replaced by one atom of oxygen. Ethylene oxide is not the only anhydride of glycol, although it is the simplest one, because $C_2H_4O = C_2H_4(OH)_2 - H_2O$. Various other anhydrides of glycol are possible, and have actually been obtained, of the composition $nC_2H_4(OH)_2 - (n-1)H_2O = (C_2H_4)_nO_{n-1}(OH)_2$. These imperfect anhydrides of glycol, or **polyglycols**, still contain hydroxyls like glycol itself, and therefore are of an alcoholic character in the same sense as glycol itself. They are obtained by various methods, and, amongst others, by the direct combination of ethylene oxide with glycol, because: $C_2H_4(OH)_2 + (n-1)C_2H_4O = (C_2H_4)_nO_{n-1}(OH)_2$. The most important circumstance, from a theoretical point of view, is that these polyglycols may be distilled without undergoing decomposition, and that the general formula given above expresses their actual molecular composition. Hence we have here a direct combination of the anhydride with the hydrate, and, moreover, a repeated one. The formula A_nH_2O may be used to express the composition of glycol and polyglycols with respect to ethylene oxide in the most simple manner, if A stand for ethylene oxide. When $n = 1$ we have glycol, when n is greater than 1 a polyglycol. Such also is the relationship of the salts of hydrate of silica, if A stand for silica, and if we imagine also that H_2O may be taken m times. Such a representation of the **polysilicic acids** corresponds with that of the polymerism of silica.

²¹ For us the latter have not a saline character only because they are not regarded from this point of view, but an alloy of sodium and zinc is, in a broad sense, a salt in many

(for instance, on cooling the alloy, or, in the case of aqueous solution, when the two metals are simultaneously liberated from the solution), definite crystalline compounds are separated. In any case there is no doubt that there is less distinction between silica and bases, than between bases and such anhydrides; as, for instance, sulphuric or nitric, or even carbonic, as is seen on comparing the physical and chemical properties of silica and various kinds of oxides. Alumina, especially, is exceedingly near akin to silica; not only in the hydrated state, but also in the anhydrous condition, there exists a certain similarity between the crystalline forms of alumina and silica in the un-

of its reactions, for it is subject to the same double decompositions as sodium phosphide or sulphide, which clearly have saline properties. The latter (sodium phosphide), when heated with ethyl iodide, forms ethyl phosphide, and the former—i.e., the alloy of zinc and sodium—gives zinc ethyl; that is, the element (P, S, Zn) which was united with the sodium passes into combination with the ethyl: $RNa + EtI = REt + NaI$. By combining sodium successively with chlorine, sulphur, phosphorus, arsenic, antimony, tin, and zinc, we obtain substances having less and less the ordinary appearance of salts, but if the alloy of sodium and zinc cannot be termed a salt, then perhaps this name cannot be given to sodium sulphide, or to the compounds of sodium with phosphorus. The following circumstance may also be observed: with chlorine, sodium gives only one compound (with oxygen, at the most three), with sulphur five, with phosphorus probably still more, with antimony naturally still more, and the more analogous an element is to sodium, the more varied are the proportions in which it is able to combine with it, the less are the alterations in the properties brought about by the combination, and the nearer does the compound formed approach to the class of compounds known as indefinite chemical compounds. In this sense a silicious alloy, containing silica and other acids, is a salt. To a certain extent the oxide plays the same part as the sodium, whilst the silica plays the part of the acid element which was taken up successively by zinc, phosphorus, sulphur, &c., in the above examples. Such a comparison of the silica compounds with alloys presents the great advantage of including under one category the definite and indefinite silica compounds—that is, brings under one head such crystalline substances as certain minerals, and such amorphous substances as are frequently met with in nature, and are artificially prepared; for example, glass, slags, enamels, &c.

If the compounds of silica are substances like the metallic alloys, then (1) the chemical union between the oxides of which they are composed must be a feeble one, as it is in all compounds formed between analogous substances. In reality such feeble agencies as water and carbonic acid are able, although slowly, to act on and destroy the majority of the complex silica compounds in rocks, as we have already seen; (2) their formation, like that of alloys, should not be accompanied by a considerable alteration of volume; and this is actually the case. For example, felspar has a specific gravity of about 2.6, and therefore, taking its composition to be $K_2O, Al_2O_3, 6SiO_2$, we find its volume, corresponding with this formula, to be $556.8 : 2.6 = 214$, the volume of $K_2O = 35$, that of $Al_2O_3 = 26$, and that of $SiO_2 = 22.6$. Hence the sum of the volumes of the component oxides, $35 + 26 + 6 \times 22.6 = 196$, which is very nearly equal to that of the felspar, so that the formation of the latter is attended by a slight expansion, and not by contraction, as happens in the majority of other cases when combinations determined by strong affinities are accomplished. In the case in question the same phenomenon is observed as in solutions and alloys—that is, as in cases of feeble affinities. So also the specific gravity of glass is directly dependent on the amount of those oxides which enter into its composition. If in the preceding example we take the sp. gr. of silica to be, not 2.65, but 2.2, its volume becomes 27.3, and the sum of the volumes will be 224—that is, greater than that of orthoclase.

combined state. Both are very hard, transparent, inactive, non-volatile, infusible, and crystallise in the hexagonal system; in a word, they are remarkably similar, and for this reason they are capable, like two kindred metals, of entering into many different degrees of combination.

Isomorphous mixtures—differing by the substitution of oxides akin both in their physical and chemical characters—are very frequently met with among minerals, and the study of the latter gave the principal impetus to the study of isomorphism. Thus, in a whole series of minerals, lime and magnesia are found in variable and interchangeable proportions. Exactly the same may be said of potassium and sodium, of alumina and ferric oxide, of manganous, ferrous, magnesium oxides, &c. Such isomorphism does not, however, extend without change of form and properties beyond certain rather narrow limits.²²

²² It is, however, easy to imagine, and experience confirms the supposition, that in a complex silicious compound containing, for instance, sodium and calcium, the whole of the sodium may be replaced by potassium, and *at the same time* the whole of the calcium by magnesium, because then the substitution of potassium for the sodium will produce a change in the nature of the substance contrary to that which will occur owing to the calcium being replaced by magnesium. That increase in weight, decrease in density, increase of chemical energy, which accompanies the exchange of sodium for potassium will, so to speak, be compensated by the exchange of calcium for magnesium, because both in weight and in properties the sum of $\text{Na} + \text{Ca}$ is very near to the sum of $\text{K} + \text{Mg}$. *Pyroxene* or *augite* can be taken as an example; its composition may be expressed by the formula $\text{CaMgSi}_2\text{O}_6$; that is, it corresponds with the acid H_2SiO_3 , and is a bisilicate. In many respects it closely resembles another mineral called *spodumene* (both being monoclinic). This latter has the composition $\text{Li}_6\text{Al}_8\text{Si}_{15}\text{O}_{45}$. On reducing both formulæ to an equal content of silica the following distinction will be observed between them: *spodumene*, $(\text{Li}_2\text{O})_6(\text{Al}_2\text{O}_3)_8, 30\text{SiO}_2$; *augite*, $(\text{CaO})_{15}(\text{MgO})_{15}, 30\text{SiO}_2$. That is, the difference between them consists in the sum of the magnesia and lime $(\text{MgO})_{15} + (\text{CaO})_{15}$ replacing the sum of the lithium oxide and alumina $(\text{Li}_2\text{O})_6 + (\text{Al}_2\text{O}_3)_8$; and in the chemical relation these sums are near to one another, because magnesium and calcium, both in forms of oxidation and in energy (as bases), in all respects occupy a position intermediate between lithium and aluminium, and therefore the sum of the first may be replaced by the sum of the second.

If we take the composition of *spodumene* to be, as it is often represented, $\text{Li}_2\text{O}, \text{Al}_2\text{O}_3, 4\text{SiO}_2$, the corresponding formula of *augite* will be $(\text{CaO})_2, (\text{MgO})_2, 4\text{SiO}_2$, and also the amount of oxygen in the sum of Li_2O and Al_2O_3 will be the same as in $(\text{CaO})_2$ and $(\text{MgO})_2$. I may remark, for the sake of clearness, that lithium belongs to the first, aluminium to the third group, and calcium and magnesium to the intermediate second group; lithium, like calcium, belongs to the even series, and magnesium and aluminium to the uneven.

The representation of the substitutions of analogous compounds here introduced (D. Mendeléeff, 1856) finds confirmation in the facts relating, for example, to the tourmalins. Wülfing (1888), on the basis of a number of analyses (especially those by Röggß), states that all varieties contain an isomorphous mixture of alkali and magnesia tourmalins; into the composition of the former there enters $12\text{SiO}_2, 3\text{B}_2\text{O}_3, 8\text{Al}_2\text{O}_3, 2\text{Na}_2\text{O}, 4\text{H}_2\text{O}$, and of the latter $12\text{SiO}_2, 3\text{B}_2\text{O}_3, 5\text{Al}_2\text{O}_3, 12\text{MgO}, 3\text{H}_2\text{O}$. Hence it is seen that the former contains the sum of $3\text{Al}_2\text{O}_3, 2\text{Na}_2\text{O}, \text{H}_2\text{O}$, which is replaced in the latter by 12MgO , in which there is as much oxygen as in the sum of the more clearly defined base $2\text{Na}_2\text{O}$, the less basic $3\text{Al}_2\text{O}_3$ and H_2O —that is, the relation is here just the same as between *augite* and *spodumene*.

What I mean by this is that lime is not always replaced totally, but often only in small quantities, by magnesia, or by manganous and ferrous oxides, without changing the crystalline form. The same may be observed with regard to potassium and lithium, which may be in part, but not completely, replaced by sodium. On the total substitution of one metal for another, the entire nature of the substance is often (although not invariably) changed; for instance, *enstatite* (or *bronzite*) is a magnesium bisilicate with a small isomorphous substitution of calcium for magnesium; its composition is expressed by the formula MgSiO_3 , and it belongs to the rhombic system. On complete substitution of calcium for magnesium, *wollastonite*, CaSiO_3 , of the monoclinic system, is obtained; when manganese is substituted, *rhodonite*, of the triclinic system, is produced; but in all of them the angles of the prism are between 86° and 88° .²³

²³ With respect to the silica compounds of the various oxides, it must be observed that only the **alkali salts** are known in a soluble form; all the others exist only in an insoluble form, so that a solution of the alkali compounds of silica, or soluble glass, gives a precipitate with a solution of the salts of the majority of other metals, and this precipitate will contain the silica compounds of the other bases. The maximum amount of the gelatinous hydrate of silica, which dissolves in caustic potash, corresponds with the formation of a compound, $2\text{K}_2\text{O}, 9\text{SiO}_2$. But this compound is partially decomposed, with the precipitation of hydrate of silica on cooling the solution. Solutions containing a smaller amount of silica may be kept for an indefinite time without decomposing, and silica does not separate out from the solution; but such compounds crystallise from the solutions with difficulty. However, a crystalline bisilicate (with water) has been obtained for sodium having the composition $\text{Na}_2\text{O}, \text{SiO}_2$ —i.e., corresponding to sodium carbonate. The whole of the carbonic acid is evolved, and a similar soluble sodium metasilicate is obtained on fusing 3.5 parts of sodium carbonate with 2 parts of silica. If less silica is taken, a portion of the sodium carbonate remains undecomposed; however, a substance may then be obtained of the composition $\text{Si}(\text{ONa})_2$, corresponding with orthosilicic acid. It contains the maximum amount of sodium oxide capable of combining with silica on fusion. It is a sodium orthosilicate, $(\text{Na}_2\text{O})_2, \text{SiO}_2$.

Calcium carbonate, and the carbonates of the alkaline earths in general, also evolve all their carbonic acid when heated with silica, and in some instances even form somewhat fusible compounds. Lime forms a fusible slag of **calcium silicate**, of the compositions CaO, SiO_2 and $2\text{CaO}, \text{SiO}_2$. With a larger proportion of silica the slags are infusible in a furnace. The magnesium **slags** are less fusible than those containing lime, and are often formed in smelting metals. Many compounds of the metals of the alkaline earths with silica are also met with in nature. For instance, among the magnesium compounds there is **olivine** $(\text{MgO})_2, \text{SiO}_2$, sp. gr. 3.4, which occurs in meteorites, and sometimes forms a precious stone (*peridot*), and is found also in slags and basalts. It is decomposed by acids, is infusible before the blowpipe, and crystallises in the rhombic system. **Serpentine**, $3\text{MgO}, 2\text{SiO}_2, 2\text{H}_2\text{O}$, sometimes forms whole mountains, and is distinguished for its great cohesiveness, being used therefore in the arts. It is generally tinted green, its specific gravity is 2.5, and it is exceedingly infusible, even before the blowpipe. It is acted on by acids. Among the magnesium compounds of silica, **talc** is very frequently met with in rocks and sometimes in compact masses; it can be used for writing like a slate pencil or chalk; and, being greasy to the touch, is also known as *steatite*. It crystallises in the rhombic system, and resembles mica in many respects; like it, it is divisible into laminae, greasy to the touch, and has a sp. gr. 2.7. These laminae are

The most remarkable complex silicious compounds are the **felspars**, which enter into nearly all the primary rocks like porphyry, granite, gneiss, &c. These felspars always contain silica, alumina, and oxides presenting marked basic properties, such as potash, soda, and lime. Thus the *orthoclase* (adularia), or ordinary felspar (monoclinic) of the granites, contains $\text{K}_2\text{O}, \text{Al}_2\text{O}_3, 6\text{SiO}_2$; *albite* contains the same substances, only with Na_2O instead of K_2O (and belongs to the triclinic system); *anorthite* contains lime, its composition being $\text{CaO}, \text{Al}_2\text{O}_3, 2\text{SiO}_2$. On expressing the last two as containing equal quantities of oxygen, we have :—

Albite	Na_2	Al_2	Si_6	O_{16}
Anorthite	Ca_2	Al_4	Si_4	O_{16}

It is then evident that, on the conversion of albite into anorthite, Na_2Si_2 is replaced by Ca_2Al_2 , and this sum, both in chemical energy and in the form of oxide, may be considered as corresponding with the first, because sodium and silicon are extreme elements in chemical character (from groups I. and IV.), and calcium and aluminium are means between them (from groups II. and III.), and actually both these felspar minerals are not only of one (triclinic) system, but form (Tschermak, Schuster) all possible kinds of definite compounds (isomorphous mixtures) among themselves, as indicated by their composition and all their properties. Thus oligoclase, andesine, labradorite, &c. (plagioclases) are nothing more than mutual combinations of albite and anorthite. Labradorite consists of albite, in combination with from 1 to 2 molecules of anorthite. The class of **zeolites** corresponds to the felspars; they are hydrated compounds of a similar composition to the felspars. Thus *natrolite* consists of $\text{Na}_2\text{O}, \text{Al}_2\text{O}_3, 3\text{SiO}_2, 2\text{H}_2\text{O}$, and *analcime* presents the same composition, but contains 4SiO_2 instead of 3SiO_2 . In general, the felspars and zeolites contain $\text{RO}, \text{Al}_2\text{O}_3, n\text{SiO}_2$, where n varies considerably.²⁴

very soft, lustrous, and transparent, and are infusible and insoluble in acids. The composition of tale approaches nearly to $6\text{MgO}, 5\text{SiO}_2, 2\text{H}_2\text{O}$.

Among the crystalline silicates the following minerals are known:—**Wollastonite** (tabular spar), which crystallises in the monoclinic system; sp. gr. 2·8; it is semi-transparent, difficultly fusible, decomposes by acids, and has the composition of a metasilicate, CaO, SiO_2 . But isomorphous mixtures of calcium and magnesium silicates occur with particular frequency in nature. The **augites** (sp. gr. 3·3), diallages, hypersthènes, hornblendes (sp. gr. 3·1), amphiboles, common asbestos, and many similar minerals, sometimes forming the essential parts of entire rock formations, contain various relative proportions of the bisilicates of calcium and magnesium partially mixed with other metallic silicates, and generally anhydrous, or only containing a small amount of water. In the pyroxenes, as a rule, lime predominates, and in the amphiboles (also of the monoclinic system), magnesia. Details must be looked for in works upon mineralogy.

²⁴ The majority of the silicious minerals have now been obtained artificially under various conditions. Thus N. N. Sokoloff showed that slags very frequently contain

Such complex silicates are generally insoluble in water,²⁵ and if they undergo change in it, it is but very slowly, and more often only

peridotite. Hautefeuille, Chroustchoff, Friedel, and Sarasin obtained felspar identical in all respects with the natural minerals. The details of the methods here employed must be looked for in special works on mineralogy; but, as an example, we will describe the method of preparation of felspar employed by Friedel and Sarasin (1881). From the fact that felspar gives up potassium silicate to water even at the ordinary temperature (Debray's experiments), they concluded that the felspar in granites had an aqueous origin (and this may be supposed to be the case from geological data); then, in the first place, its formation could not be accomplished except in the presence of an excess of potassium silicate solution. In order to render this argument clear I may mention, as an example, that carnallite is decomposed by water into easily soluble magnesium chloride and potassium chloride, and therefore if it is of aqueous origin it could not be formed otherwise than from a solution containing an excess of magnesium chloride, and, in the second place, from a strongly heated solution; again, felspar itself and its fellow-components in granites are anhydrous. On these facts were based experiments of heating hydrates of silica with alumina and a solution of potassium silicate in a closed vessel. The mixture was placed in a sealed platinum tube, which was enclosed in a steel tube and heated to dull redness. When the mixture contained an excess of silica the residue contained many crystals of rock crystal and tridymite, together with a powder of felspar, which formed the main product of the reaction when the proportion of hydrate of silica was decreased, and a mixture of a solution of potassium silicate with alumina precipitated together with the silica by mixing soluble glass with aluminium chloride was employed. The composition, properties, and forms of the resultant felspar proved it to be identical with that found in nature. The experiments approach very nearly to the natural conditions, all the more so since felspar and quartz are obtained together in one mixture, as they so often occur in nature.

²⁵ The application of **cements** is based on this principle: they are those sorts of 'hydraulic' lime which generally form a stony mass, which hardens, even under water, when mixed with sand and water.

The hydraulic properties of cements are due to their containing calcareous and silico-aluminous compounds capable of combining with water and forming hydrates, which are then unacted on by water. This is best proved, in the first place, by the fact that certain slags containing lime and silica, and obtained by fusion (for example, in blast-furnaces), solidify like cements when finely ground and mixed with water; and, in the second place, by the method now employed for the manufacture of artificial cements (formerly only peculiar and comparatively rare natural products were used). For this purpose a mixture of lime and clay is taken, containing about 25 per cent. of the latter; this mixture is then heated, not to fusion, but until both the carbonic anhydride and water contained in the clay are expelled. This mass when finely ground forms Portland cement, which hardens under water. The process of hardening is based on the formation of chemical compounds between the lime, silica, alumina, and water. These substances are also found combined together in various natural minerals—for example, in the zeolites, as we saw above. In all cases cement which has set contains a considerable amount of water, and its hardening is naturally due to hydration—that is, to the formation of compounds with water. Well-prepared and very finely ground cement hardens comparatively quickly (in several days, especially after being rammed down), with 3 parts (and even more) of coarse sand and with water, into a stony mass which is as hard and durable as many stones, and more so than bricks and limestone. Hence not only all maritime constructions (docks, ports, bridges, &c.), but also ordinary buildings, are made of Portland cement, and are distinguished for their great durability. A combination of ironwork (ties, girders) and cement (Monier) is particularly suitable for the construction of aqueducts, arches, reservoirs, &c. Arches and walls made of such cements may be much less thick than those built up of ordinary stone. Hence the production and use of cement increase rapidly from year to year. The origin of accurate data respecting

takes place in the presence of carbonic acid. Some of the silicates which are insoluble in water are easily and directly decomposed by acids; for instance, the zeolites and those fused silicates which contain a large quantity of energetic bases such as lime. Many of the silicates, like glass,²⁶ are hardly changed by acids, particularly if they contain

cements is chiefly due to Vicat. In Russia Professor Schuliachenko has greatly aided the extension of accurate data concerning Portland cement. Many works for the manufacture of cement have already been established in various parts of Russia, and this industry promises a great future in the arts of construction.

²⁵ **Glass** presents a complex composition similar to that of many minerals. The ordinary sorts of white glass contain about 75 per cent. of silica, 13 of sodium oxide, and 12 of lime; but some sorts of glass contain as much as 10 per cent. of alumina. The mixtures which are used for the manufacture of glass are also most varied. For example, about 300 parts of pure sand, 100 of sodium carbonate, and 50 of limestone are taken, and sometimes double the proportion of the latter. Ordinary **soda-glass** contains sodium oxide, lime, and silica as the chief component parts. It is generally prepared from sodinm sulphate mixed with charcoal, silica, and lime (Chap. XII.), in which case the following reaction takes place at a high temperature: $\text{Na}_2\text{SO}_4 + \text{C} + \text{SiO}_2 = \text{Na}_2\text{SiO}_3 + \text{SO}_2 + \text{CO}$. Sometimes potassium carbonate is taken for the preparation of the better qualities of glass. In this case a glass, **potash-glass**, is obtained containing potassium oxide instead of sodium oxide. The best-known of these glasses is the so-called Bohemian glass or crystal, which is prepared by the fusion of 50 parts of potassium carbonate, 15 parts of lime, and 100 parts of quartz. The preceding kinds of glass contain lime, whilst crystal glass contains lead oxide instead. Flint glass—that is, the lead glass used for optical instruments—is prepared in this manner, naturally from the purest possible materials. *Crystal-glass*—i.e., glass containing lead oxide—is softer than ordinary glass, more fusible, and has a higher index of refraction. Borax is sometimes added to glass to render it more fusible, and suboxide of thallium to increase the index of refraction (especially in paste). However, although the materials for the preparation of glass may be most carefully sorted, a certain amount of iron oxides gets into the glass and renders it greenish. This coloration may be destroyed by adding to the vitreous mass one of a number of substances which are able to convert the ferrous oxide into ferric oxide; for example, manganese peroxide (because the peroxide is deoxidised to manganous oxide, which only gives a pale violet tint to the glass) and arsenious anhydride, which is deoxidised to arsenic, and this is volatilised. The manufacture of glass is carried on in furnaces giving a very high temperature (often in regenerator furnaces, Chap. IX.). Large stone or clay crucibles are placed in these furnaces, and the mixture destined for the preparation of the glass, having been first roasted, is charged into the crucibles. The temperature of the furnace is then gradually raised. The process takes place in three separate stages. At first the mass intermixes and begins to react; then it fuses, evolves carbonic acid gas, and forms a molten mass; and, lastly, at the highest temperature, it becomes homogeneous and quite liquid, which is necessary for the ultimate elimination of the carbonic anhydride and solid impurities, which latter collect at the bottom of the crucible. The temperature is then lowered somewhat, and the glass is taken out on tubes and blown into objects of various shapes. In the manufacture of window-glass it is blown into large cylinders, which are then cut at the ends and across, and afterwards bent back in a furnace into the ordinary sheets. After being worked up, all glass objects have to be subjected to a slow cooling (*annealing*) in special furnaces, otherwise they are very brittle, as is seen in the so-called ‘Rupert’s drops,’ formed by dropping molten glass into water; although these drops are very hard and preserve their form, they break up into a fine powder if a small piece be knocked off them, owing to the great internal strain. In the manufacture of mirrors and many massive objects the glass is cast and then ground and polished. Coloured glasses are made either by directly introducing into the glass itself various oxides, which give their

much silica, whilst fusion with alkalis leads to the formation of compounds rich in bases, after which acids decompose the alloys formed.²⁷

According to the periodic law, the nearest analogues of silicon ought to be elements of the uneven series, because silicon, like sodium, magnesium, and aluminium, belongs to this series.²⁵ Immediately after silicon follows ekasilicon or germanium, $\text{Ge}=72$, whose properties were predicted (1871) before Winkler (1886) in Freiberg, Saxony (Chap. XV. § 5), discovered this element in a peculiar silver ore called *argyrodite*, Ag_6GeS_5 .²⁹ Easily reduced from the oxide by heating with hydrogen and charcoal, and separated from its solutions by zinc,

characteristic tints, or else a thin layer of a coloured glass is laid on the surface of ordinary glass. Green glasses are formed by the oxides of chromium and copper, blue by cobalt oxide, violet by manganese oxide, and red glass by cuprous oxide and by the so-called purple of Cassius—i.e., a compound of gold and tin—which will be described later. A yellow coloration is obtained by means of the oxides of iron, silver, or antimony, and also by means of carbon, especially for the brown tints for certain kinds of bottle-glass.

From what has been said about glass, it will be understood that it is impossible to give a definite formula for it, because it is a non-crystalline or amorphous alloy of silicates; but such an alloy can only be formed within certain limits in the proportions between the component oxides. With a large proportion of silica the glass very easily becomes clouded when heated; with a considerable proportion of alkalis it is easily acted on by moisture, and becomes cloudy in time on exposure to the air; with a large proportion of lime it becomes infusible and opaque, owing to the formation of crystalline compounds in it; in a word, a certain proportion is practically attained among the component oxides in order that the glass formed may have suitable properties. Nevertheless, it may be well to remark that the composition of good sorts of glass approaches to the formula, $\text{Na}_2\text{O}, \text{CaO}, 6\text{SiO}_2$.

The coefficient of cubical expansion of glass is nearly equal to that of platinum and iron, being approximately 0.000027. The specific heat of glass is nearly 0.18, and the specific gravity of common soda glass nearly 2.5, that of Bohemian glass 2.4, and that of bottle glass 2.7. Flint glass is much heavier than common glass, because it contains the heavier oxide of lead, its specific gravity being 2.9 to 3.2. Further details will be found in text-books of technology.

²⁷ It must be recollected that although acids seem to act only feebly on the majority of silicates, nevertheless a finely levigated powder of silicious compounds is acted on by strong acids, especially with the aid of heat, the basic oxides being taken up and gelatinous silica left behind. In this respect sulphuric acid heated to 200° with finely divided silicious compounds in a closed tube acts very energetically.

²⁸ Such elements as silicon, tin, and lead were only brought together under one common group by means of the periodic law, although the quadrivalency of tin and lead was known much earlier. Generally silicon was placed among the non-metals, and tin and lead among the metals.

²⁹ At first (February 1886) the want of material to work on, the absence of a spectrum in the Bunsen's flame, and the solubility of many of the compounds of germanium, presented difficulties in the researches of Professor Winkler, who, on analysing argyrodite by the usual method, obtained a constant loss of 7 per cent., and was thus led to search for a new element. The presence of arsenic and antimony in the accompanying minerals also impeded the separation of the new metal. After fusion with sulphur and sodium carbonate, argyrodite gives a solution of a sulphide which is precipitated by an excess of hydrochloric acid; germanium sulphide is soluble in ammonia and is then precipitated by hydrochloric acid, as a white precipitate, which is dissolved

metallic germanium proved to be greyish white, easily crystallisable (in octahedra), brittle, fusible (under a coating of fused borax) at about 900° , and easily oxidisable; the specific gravity = 5.469, the atomic weight = 72.3, and the specific heat = 0.076,³⁰ as might be expected for this element according to the periodic law. The corresponding **germanium dioxide**, GeO_2 , is a white powder having a specific gravity of 4.703; water, especially when boiling, dissolves this dioxide (1 part of GeO_2 requires for solution 247 parts of water at 20° , 95 parts at 100°). It forms soluble salts with alkalis and is but sparingly soluble in acids.³¹ In a stream of chlorine the metal forms **germanium chloride**, GeCl_4 , which boils at 86° , and has a specific gravity of 1.887 at 18° ; water decomposes it, forming the oxide. All these properties³² of germanium, showing its analogy to silicon and tin, form a most beautiful demonstration of the truth of the periodic law.³³

(or decomposed) by water. After being oxidised by nitric acid, dried and ignited germanium sulphide leaves the oxide GeO_2 , which is reduced to the metal when ignited in a stream of hydrogen.

³⁰ G. Kobb determined the spectrum of germanium. The wave-lengths of the most distinct lines are given in Chap. XIII.

³¹ If germanium or its sulphide is heated in a stream of hydrochloric acid, it forms a volatile liquid, boiling at 72° , which corresponds to germanium chloroform, GeHCl_3 . It is decomposed by water, forming a basic salt of the hydrate of the suboxide, GeO , which acts as a powerful reducing agent in hydrochloric acid solution. After prolonged heating with a solution of NaHO in large excess (about 5 NaHO per GeHCl_3), all the suboxide passes into the solution, which, on the one hand, resembles the alkaline solutions of the hydrates of ZnO , PbO , Al_2O_3 , SiO_2 , and, on the other, bears some analogy to sodium formate, CHNaO_2 , which is equivalent to $\text{CO} + \text{NaHO}$, while the germanium solution is $\text{GeO} + \text{NaHO}$; and this solution (Hantzsch, 1902), after being saponified with ethyl aceto-acetate and treated carefully with sufficient HCl to saturate all the alkali, gives an acid solution of GeH_2O_2 , which may be regarded as either germanoformic acid or as the hydrosol (colloid solution) of hydrated suboxide of germanium, $\text{GeO}, \text{H}_2\text{O}$.

Voegelen (1902) showed that if chloride of germanium is added to sulphuric acid acting on zinc, it is partially converted (like As and Sb) into a volatile (gaseous) *hydride*, which when heated deposits metallic germanium, like arseniuretted hydrogen, in a thin mirror-like layer, which is grey by reflected and reddish by transmitted light. Judging from its reaction with sulphur (under the action of light), it has the composition GeH_4 , and the reaction proceeds according to the equation, $\text{GeH}_4 + \text{S}_4 = \text{GeS}_2 + 2\text{H}_2\text{S}$.

³² Under certain circumstances germanium gives a blue coloration like that of ultramarine, as Winkler showed, which might have been expected from the analogy of germanium with silicon.

³³ Winkler expressed this in the following words (*Jour. f. prakt. Chemie*, 1886, 34, 182-183): ‘ . . . es kann keinem Zweifel mehr unterliegen, dass das neue Element nichts Anderes, als das vor fünfzehn Jahren von *Mendeléeff* prognosticirte *Ekasilicium* ist.’

‘Denn einen schlagenderen Beweis für die Richtigkeit der Lehre von der Periodicität der Elemente, als den, welchen die Verkörperung des bisher hypothetischen “Eka-siliciums” in sich schliesst, kann es kaum geben, und er bildet in Wahrheit mehr, als die blosse Bestätigung einer kühn aufgestellten Theorie, er bedeutet eine eminente Erweiterung des chemischen Gesichtsfeldes, einen mächtigen Schritt in’s Reich der Erkenntniss.’

The increase of atomic weight from silicon 28 to germanium 72 is 44—that is, about the same difference as there is in the atomic weights of chlorine and bromine ; between germanium and its next analogue, tin ($\text{Sn}=119$), the difference is 47—that is, almost as much as the amount by which the atomic weight of iodine exceeds that of bromine.

Metallic tin is rarely met with in **nature** ; it occurs in the veins of ancient formations, almost exclusively in the form of oxide, SnO_2 , called **tin-stone**. The best known tin deposits are in Cornwall and in Malacca. In Russia, tin ores have been found in small quantities on the shores of Lake Ladoga, in Pitkarand. The crushed ore may easily be separated from the earthy matter accompanying it by washing on inclined tables, as the tin-stone has a specific gravity of 6.9, whilst the impurities are much lighter. **Tin oxide is very easily reduced** to metallic tin by heating with charcoal. For this reason tin was known in ancient times, and the Phœnicians brought it from England. Metallic tin is cast into ingots of considerable weight or into thin sticks or rods. Tin has a white colour, rather duller and more blue than that of silver. It fuses easily at 232° , and crystallises on cooling. Its specific gravity is 7.2. The crystalline structure of ordinary tin is noticed in bending tin rods, when a peculiar sound is heard, produced by the fracture of the particles of tin along the surfaces of crystalline structure.

When pure tin is cooled to a low temperature it splits up into separate crystals, the bond between the particles is lost, the tin assumes a grey colour, becomes less brilliant—in a word, its properties become changed, as was shown by Fritzsche. This depends on the different structure (allotropic, dimorphous) which the tin then acquires, and is particularly remarkable because it is effected by cold in a solid.^{33a} If such grey tin is fused, or even simply heated above 20° , it becomes like ordinary tin, but is again changed when cooled. If tin is powdered (see further on ; tin becomes very brittle at about 200° and may then be reduced to a powder in a mortar) and moistened with a solution of tin in hydrochloric acid, it passes from the ordinary form into the grey variety with comparative ease. The transition temperature lies at about 20° (Cohen and van Dyk), the grey variety being formed below and the ordinary one above this temperature ; still the conversion from one into the other variety proceeds slowly at temperatures about $+20^\circ$, but at -40° or -50° the grey tin is rapidly formed. Its specific gravity is generally below that of ordinary tin, and sometimes even as low as 5.8.³⁴

^{33a} Emilianoff (1890) states that in the cold of the Russian winter 30 out of 200 tin moulds for candles were spoilt through becoming quite brittle.

³⁴ The tin deposited by the electric current from solutions of SnCl_2 appears in

Tin is softer than silver or gold, and is only surpassed by lead in this respect. In addition to this it is very ductile, but its tenacity is very slight, so that wire made from it will bear but little strain. In consequence of its ductility it is easily worked, by forging and rolling into very thin sheets (tin foil), which are used for wrapping round many articles to preserve them from the action of moisture, &c. In this case, however, and in many others, lead is mixed with the tin, which, within certain limits, does not alter the ductility. Although so soft at the ordinary temperatures, tin becomes brittle at 200° before fusing. Tin powder may be easily obtained if the metal be fused and then stirred while cooling. At a white heat tin may be distilled, but with more difficulty than zinc. If molten tin comes into contact with oxygen, it oxidises, forming stannic oxide, SnO_2 , and its vapour burns with a white flame. **At ordinary temperatures tin does not oxidise**, and this very important property of tin allows it to be applied in many cases for covering other metals to prevent their oxidising. This is termed **tinning**. Iron and copper are frequently tinned. Iron and steel sheets, coated with tin, bear the name of tin plate (for the most part made in England), and are used for numerous purposes.^{34a}

Tin with copper forms **bronze**, an alloy which is most extensively used in the arts. Bronze has various colours and a variety of physical properties, according to the relative amount of copper and tin which it contains. With an excess of copper the alloy has a yellow colour; the admixture of tin imparts considerable hardness and elasticity to the copper. An alloy containing 78 parts of copper and about 22 per cent. of tin is so elastic that it is used for casting bells, which naturally require a very elastic and hard alloy.³⁵ For casting crystals of the cubic system, and has a specific gravity of 7.8, which is less than that of ordinary tin. The tin deposited by an electric current from a neutral solution of SnCl_2 readily oxidises and becomes coated with SnO (Vignon, 1889).

^{34a} Tin plate is prepared by immersing iron sheets, previously thoroughly cleansed by acid and mechanical means, in molten tin. If after this the coating of tin be rapidly cooled—for instance, by dashing water over it—it crystallises in diverse star-shaped figures, which become visible when the sheets are first immersed in dilute aqua regia and then in a solution of caustic soda.

The coating of iron by tin guards it against the direct access of air, but it only preserves the iron from oxidation so long as it forms a perfectly continuous coating. If the iron is left bare in certain places, it will be powerfully oxidised at these spots, because the tin is electro-negative with respect to the iron, and thus the oxidation is confined entirely to the iron in the presence of tin. However, a dense and invariable alloy is formed over the surface of contact of the iron and tin, which binds the coating of tin to the remaining mass of the iron. Tin may be fused with cast iron. The coating of copper objects by tin is generally done to preserve the copper from the action of acid liquids, which would attack the copper in the presence of air and convert it into poisonous salts. Tin is not acted on in this manner, and therefore copper vessels for the preparation of food should be tinned.

³⁵ The ancient Chinese alloys containing about 20 per cent. of tin (specific gravity of

statues and various large or small ornamental articles alloys containing 2 to 5 per cent. of tin, 10 to 30 per cent. of zinc, and 65 to 85 per cent. of copper, are used.³⁶ Tin is also often used alloyed with lead, for making various objects—for instance, drinking vessels.

Tin decomposes the vapour of water when heated with it, liberating the hydrogen and forming stannic oxide. Sulphuric acid, diluted with

alloys about 8·9), which have been rapidly cooled, are distinguished for their resonance and elasticity. These alloys were formerly manufactured in large quantities in China for the musical instruments known as *tom-toms*. Owing to their hardness, alloys of this nature are also employed for casting guns, bearings, &c., and an alloy containing about 11 per cent. of tin is known as gun-metal. The addition of a small quantity of phosphorus, up to 2 per cent., renders bronze still harder and more elastic, and the alloy so formed is now used under the name of phosphor-bronze.

The alloy SnCu_3 (58·3 per cent. of Cu) is brittle, of a *bluish* colour, and has nothing in common with either copper or tin in its appearance or properties. It remains perfectly homogeneous on cooling, and acquires a crystalline structure (Riche). These signs clearly indicate that the alloy SnCu_3 is a product of chemical combination, which is also seen to be the case from its density—namely, 8·91, which is greater than that of copper. Had there been no contraction, the density of the alloy would be 8·21. It is the heaviest of all the alloys of tin and copper, the density of tin being 7·29 and that of copper 8·8. The alloy SnCu_4 , specific gravity 8·77, has similar properties (according to Riche). All the alloys except SnCu_3 (and SnCu_4) split up on cooling; a portion richer in copper solidifies first (this phenomenon is termed the *liquation* of an alloy), but the above two alloys do not split up on cooling. In these and many similar facts we can clearly distinguish a **chemical union between the metals** forming an alloy. The formation of the definite alloy SnCu_3 , discovered by Riche on the basis of his researches on the densities (the density of this alloy differs considerably, according to whether it is cast or in filings; it was not determined in a molten state), was most clearly confirmed by Laurie's researches on the electro-motive force of the alloys, as this was found to be nearly the same as that of Sn or Cu before and after Cu_3Sn , and to give a marked rise for the alloy Cu_3Sn . The electrical conductivity of the alloys also exhibits a critical point for Cu_3Sn . The most fusible or eutectic (Chap. I., note 58) of the alloys rich in copper apparently has a composition about Cu_5Sn or contains 72·7 per cent. of copper. The alloys of tin and copper were known in very remote ages, before iron was used. The alloys of zinc and tin are less used, but alloys composed of zinc, tin, and copper frequently replace the more costly bronze. Concerning the alloys of lead, see note 46.

³⁶ An excellent proof of the fact that alloys and solutions are subject to law is given, amongst others, by the application of Raoult's method of freezing-point depression (Chap. I., note 49, and Chap. VII.) to solutions of different metals in tin. Thus, Heycock and Neville (1889) showed that the temperature of solidification of molten tin (226·4°) is always lowered by the presence of a small quantity of another metal in proportion to the concentration of the solution. The following were the reductions of the temperature of solidification of tin obtained by dissolving 11,900 parts of it in atomic proportions of different metals (for example, 65 parts of zinc); Zn 2·53°, Cu 2·47°, Ag 2·67°, Cd 2·16°, Pb 2·6°, Hg 2·3°, Sb 2·3° [rise], Al 1·34°. As this method (Chap. VII.) enables the molecular weight to be determined, the almost perfect identity of the resultant figures (except for aluminium) shows that the molecules of copper, silver, lead, and antimony contain *one atom in the molecule*, like zinc, mercury, and cadmium. They obtained the same result (1890) for Mg, Na, Ni, An, Pd, Bi, and In. It should here be mentioned that for the same purpose (the determination of the molecular weight of metals on the basis of their mutual solution), Ramsay (1889) took advantage of the variation of the vapour pressure of mercury (Chap. VII.) containing various metals in solution, and he also found that the above-mentioned metals contain but one atom in the molecule.

a considerable quantity of water, does not act, or at all events does so only very slightly, on tin, but tin reduces hot strong sulphuric acid, when not only sulphurous anhydride but also sulphuretted hydrogen is evolved. Hydrochloric acid acts very readily on tin, with evolution of hydrogen and formation of stannous chloride, SnCl_2 , in solution, which, with an excess of hydrochloric acid and access of air, is converted into stannic chloride or tetrachloride of tin: $\text{SnCl}_2 + 2\text{HCl} + \text{O} = \text{SnCl}_4 + \text{H}_2\text{O}$.^{36a} Nitric acid diluted with a considerable quantity of water dissolves tin at the ordinary temperature, while the nitric acid itself is reduced, forming, amongst other products, ammonia and hydroxylamine. Here the tin passes into solution in the form of stannous nitrate. Stronger nitric acid (also more dilute, when heated) transforms the tin into its highest grade of oxidation, SnO_2 , but the latter then appears as the so-called metastannic acid, which does not dissolve in nitric acid, and therefore the tin does not pass into solution. Feeble acids—for instance, carbonic and organic acids—do not act on tin even in the presence of oxygen, because tin does not form any powerful bases.

It is important to remark as a characteristic of tin, that it is reduced from its solutions by many metals which are more easily oxidised, as, for instance, by zinc.

In combination, tin appears in the two forms, SnX_4 and SnX_2 , compounds of the intermediate type, Sn_2X_6 , being also known, but these latter pass with remarkable facility in most cases into compounds of the higher and lower types, and therefore the form SnX_3 ³⁷ cannot be considered as independent.

Stannous oxide, SnO , in an anhydrous condition is obtained by boiling solutions of stannous salts with alkalies, the first action of the alkali being to precipitate a white hydrate of stannous oxide, $\text{Sn}(\text{OH})_2$, SnO . The latter when heated parts with water as easily as the hydrate of copper oxide. In this form, stannous oxide is a black crystalline powder (specific gravity 6.7) capable of further oxidation when heated. The

^{36a} The action of hydrochloric acid on tin forms an excellent means of reducing, wherein both the hydrogen liberated by the mixture (at the moment of separation) and the stannous chloride act as powerful reducing and deoxidising agents. Thus, for instance, by this mixture nitro-compounds are transformed into amido-compounds—that is, the elements of the group NO_2 are reduced to NH_2 .

³⁷ Many volatile compounds of tin are known, the molecular weights of which can therefore be established from their vapour densities. Among these may be mentioned stannic chloride, SnCl_4 , and stannic ethide, $\text{Sn}(\text{C}_2\text{H}_5)_4$, (the latter boils at about 150°). But V. Meyer found the vapour density of stannous chloride, SnCl_2 , to be variable between its boiling-point (606°) and 1100° , owing, it would seem, to the fact that the molecule then varies from Sn_2Cl_4 to SnCl_2 ; but the vapour density proved to be less than that indicated by the first and greater than that shown by the second formula, although it approaches to the latter as the temperature rises.

hydrate is freely soluble in acids, and also in potassium and sodium hydroxides, but not in aqueous ammonia.³⁸ This property indicates the feeble basic properties of this lower oxide, which acts in many cases as a reducing agent.³⁹ Among the compounds corresponding with stannous oxide the most remarkable and the one most frequently used is stannous chloride or **chloride of tin**, SnCl_2 , also called protochloride of tin (because it is the lowest chloride, containing half as much Cl as SnCl_4). It is a transparent, colourless, crystalline substance, melting at 250° and boiling at 606° . Water dissolves it, without visible change (in reality partial decomposition occurs, as we shall see presently). It is also soluble in alcohol. It is obtained by heating tin in dry hydrochloric acid gas, the hydrogen being then liberated, or by dissolving metallic tin in hot strong hydrochloric acid and then evaporating quickly. On cooling, crystals of the monoclinic system are obtained having the composition $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$. An aqueous solution of this substance absorbs oxygen from the atmosphere and gives a precipitate containing stannic oxide. From this it follows that a solution of stannous chloride will act as a reducing agent; a fact frequently made use of in chemical investigations—for example, for reducing metals from their solutions—since even mercury may be reduced to a metallic state from its salts by means of stannous chloride. This reducing property is also employed in the arts, especially in the dyeing industry, where this substance in the form of a crystalline salt finds an extensive application, and is known as *tin salt* or tin crystals.

Stannic oxide, SnO_2 , occurring in nature as *tinestone*, or *cassiterite*, is formed, during the oxidation or combustion of heated tin in air, as a white or yellowish powder which fuses with difficulty. It is prepared

³⁸ When rapidly boiled, an alkaline solution of stannous oxide deposits tin and forms stannic oxide, $2\text{SnO} = \text{Sn} + \text{SnO}_2$, which remains in the alkaline solution.

³⁹ Weber (1882), by precipitating a solution of stannous chloride with sodium sulphite (this salt, as a reducing agent, prevents the oxidation of the stannous compound) and dissolving the washed precipitate in nitric acid, obtained crystals of *stannous nitrate*, $\text{Sn}(\text{NO}_3)_2 \cdot 20\text{H}_2\text{O}$, on refrigerating the solution. This crystallo-hydrate easily melts, and is deliquescent. Besides this, a more stable anhydrous basic salt, $\text{Sn}(\text{NO}_3)_2 \cdot \text{SnO}$, is easily formed. In general, stannous oxide, as a feeble base, readily forms basic salts, just as cupric and lead oxides do. For the same reason SnX_2 easily forms double salts. For instance, a potassium salt, $\text{SnK}_2\text{Cl}_4 \cdot \text{H}_2\text{O}$, and especially an ammonium salt, $\text{Sn}(\text{NH}_4)_2\text{Cl}_4 \cdot \text{H}_2\text{O}$, called **pink salt**, are known. Some of these salts are used in the arts, owing to their being more stable than tin salts alone. Stannous bromide and iodide, SnBr_2 and SnI_2 , resemble the chloride in many respects.

Among other stannous salts a sulphate, SnSO_4 , is known. It is formed as a crystalline powder when a solution of stannous oxide in sulphuric acid is evaporated under the receiver of an air-pump. It decomposes, when heated, into stannic oxide and sulphurous anhydride.

In gaseous hydrochloric acid, stannous chloride, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, forms a liquid having the composition, $\text{SnCl}_2 \cdot \text{HCl} \cdot 3\text{H}_2\text{O}$ (sp. gr. 2.2, freezes at -27°).

in large quantities, being used as a white vitreous mixture for coating ordinary tiles and similar earthenware objects with a layer of easily fusible glass or enamel. Acid solutions of stannic oxide treated with alkalis, and alkaline solutions treated with acids, give a precipitate of stannic hydroxide, $\text{Sn}(\text{OH})_4$, also known as stannic acid, which, when heated, gives up water and leaves the anhydride, SnO_2 , which is insoluble in acids, clearly showing the feebleness of its basic character. When fused with alkali hydroxides (not with their carbonates or acid sulphates), an alkaline compound is obtained which is soluble in water. Stannic hydroxide, like the hydrates of silica, is a colloidal substance, and presents several different modifications, depending on the method of preparation, but having an identical composition; the various hydroxides have also a different appearance, and act differently with reagents. For instance, a distinction is made between ordinary stannic acid and metastannic acid. **Stannic acid** is produced by precipitation by soda or ammonia from a freshly prepared solution of stannic chloride, SnCl_4 , in water; on drying the precipitate thus obtained, a non-crystalline mass is formed, which is freely soluble in strong hydrochloric or nitric acid, and also in potassium or sodium hydroxide. This ordinary stannic acid may be still better obtained from sodium stannate by the action of acids. **Metastannic acid** is insoluble in sulphuric or nitric acid. It is obtained in the form of a heavy white powder by treating tin with nitric acid; hydrochloric acid does not dissolve it immediately, but changes it to such an extent that, after pouring off the acid, water extracts the stannic chloride, SnCl_4 , already formed. Dilute alkalis not only dissolve metastannic acid, but also transform it into salts, which slowly, yet completely, dissolve *in pure water*, but are insoluble even in dilute alkali hydroxides. Dilute hydrochloric acid, especially when boiling, changes the ordinary hydrate into metastannic acid. On this depends, by the way, the formation of a white precipitate, stannic hydroxide, from solutions of stannous and stannic chlorides diluted with water. The stannic oxide first dissolved changes under the influence of hydrochloric acid into metastannic acid, which is insoluble in water in the presence of hydrochloric acid. Solutions of metastannic acid differ from solutions of ordinary stannic acid, and in the presence of alkali they change into solutions of ordinary acid, so that metastannic acid corresponds principally with the acid compounds of stannic oxide, and ordinary stannic acid with the alkaline compounds.⁴⁰ Graham

⁴⁰ Frémy supposes the cause of the difference to consist in polymerisation, and considers that the ordinary acid corresponds with the oxide SnO_2 , and the meta-acid with the oxide Sn_2O_3 , but it is more probable that both are polymeric, though to a different

obtained a soluble colloidal hydroxide ; it is subject to the same transformations as are in general peculiar to colloids.

Stannic oxide shows the properties of a slightly energetic and intermediate oxide (like water, silica, &c.) ; that is to say, it forms saline compounds both with bases and with acids, but both are easily decomposed, and are but slightly stable. But still the acid character is more clearly developed than the basic, as in silica, germanic oxide, and lead dioxide. This determines the character of the compounds SnX_4 , corresponding to **stannic chloride**, SnCl_4 or tetrachloride of tin. It is obtained in an anhydrous condition by the direct action of chlorine on tin, and is then easily purified, as it is a liquid boiling at 114° . Its specific gravity is 2.28 (at 0°), and it fumes in the open air (*spiritus fumans Libavii*), reacting on the moisture of the air, and thus showing the properties of a chloranhydride. Water, however, does not at first decompose it, but dissolves it, and on evaporation gives the crystallohydrate, $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$. If but little water is taken, crystals containing $\text{SnCl}_4 \cdot 3\text{H}_2\text{O}$ are formed, which part with one-third of their water when placed under the receiver of an air-pump. A large quantity of water, however, especially on heating, gives rise to a precipitate of metastannic acid ⁴¹ and to formation of HCl .

degree. Stannic acid with sodium carbonate gives a salt of the composition Na_2SnO_3 . The same salt is also obtained by fusing metastannic acid with sodium hydroxide, whilst metastannic acid gives a salt, $\text{Na}_2\text{SnO}_3 \cdot 4\text{SnO}_2$ (Frémy), when treated with a dilute solution of alkali ; moreover, stannic acid is also soluble in the ordinary stannate, Na_2SnO_3 (Weber), so that both stannic acids (like both forms of silica) are capable of polymerisation, and probably only differ in its degree. In general, there is here a great resemblance to silica, and Graham obtained a solution of stannic acid by the direct dialysis of its alkaline solution. The main difference between these acids is that the meta-acid is soluble in hydrochloric acid, and gives a precipitate with sulphuric acid and stannous chloride, which do not precipitate the ordinary acid. Vigon (1889) found that more heat is evolved in dissolving stannic acid in KHO than metastannic. The polymerisation of many oxides, for example, of ZnO , CaO , Bi_2O_3 , &c., must be recognised on the basis of the formation of the polyhydrates $(\text{RO})_2\text{H}_2\text{O}$, and in general this is very likely an exceedingly common phenomenon, but it is most probably of all the case with oxide of tin.

⁴¹ The formation of the compound $\text{SnCl}_4 \cdot 3\text{H}_2\text{O}$ is accompanied by so great a contraction that these crystals, although they contain water, are heavier than the anhydrous chloride SnCl_4 . The pentahydrated crystallo-hydrate absorbs dry hydrochloric acid, and gives a liquid of specific gravity 1.971, which at 0° yields crystals of the compound $\text{SnCl}_4 \cdot 2\text{HCl} \cdot 6\text{H}_2\text{O}$ (it corresponds with the similar platinum compound), which melt at 20° into a liquid of specific gravity 1.925 (Engel).

Stannic chloride combines with ammonia ($\text{SnCl}_4 \cdot \text{NH}_3$), hydrocyanic acid, phosphoretted hydrogen, phosphorus pentachloride ($\text{SnCl}_4 \cdot \text{PCl}_5$), nitrous anhydride and its chloranhydride ($\text{SnCl}_4 \cdot \text{N}_2\text{O}_3$ and $\text{SnCl}_4 \cdot 2\text{NOCl}$), and with metallic chlorides (for example, $\text{K}_2\text{SnCl}_6 \cdot (\text{NH}_4)_2\text{SnCl}_6$, &c.). In general, a highly developed faculty for combination is observed in it.

Tin does not combine directly with iodine, but if its filings are heated in a closed tube with a solution of iodine in carbon bisulphide, it forms stannic iodide, SnI_4 , in the form of red octahedra which fuse at 142° and volatilise at 295° . The fluorine compounds of

The alkali compounds of stannic oxide—that is, the compounds in which SnO_2 plays the part of an acid, corresponding with the compounds of silica—are very easily formed and are used in the arts. Their composition in most cases corresponds with the formula SnM_2O_3 —that is, $\text{Sn}(\text{MO})_2$, similar to $\text{CO}(\text{MO})_2$, where $\text{M}=\text{K}, \text{Na}$. Acids, even feeble ones like carbonic acid, decompose the salts, like the corresponding compounds of alumina or silica. In order to obtain *potassium stannate*, which crystallises in rhombohedra, and has the composition $\text{SnK}_2\text{O}_3, 3\text{H}_2\text{O}$, potassium hydroxide (8 parts) is fused, and metastannic acid (3 parts) gradually added. **Sodium stannate** is prepared in practice in large quantities by heating a solution of caustic soda with lead oxide and metallic tin. In this last case an alkaline solution of lead oxide is formed, and the tin acts on the solution in such a way as to reduce the lead and pass into solution. It is very remarkable that lead displaces tin when in combination with acids, whilst tin, on the contrary, displaces lead from its alkali compounds. By dissolving the mass obtained in water, and adding alcohol, sodium stannate is precipitated, and may then be dissolved in water and purified by re-crystallisation. The crystals have the composition $\text{SnNa}_2\text{O}_3, 3\text{H}_2\text{O}$ if separated from hot strong solutions, and $\text{SnNa}_2\text{O}_3, 10\text{H}_2\text{O}$ when crystallised at a low temperature. This salt is used as a mordant in dyeing operations. With a cold solution of sodium hydroxide, metastannic acid forms a salt of the composition $(\text{NaHO})_2, 5\text{SnO}_2, 3\text{H}_2\text{O}$, from which Frémy drew his conclusions concerning the polymerism of metastannic acid. Like

tin have a special interest in the history of chemistry, because they give a series of double salts which are isomorphous with the hydrofluosilicates, SiR_2F_6 , and this fact served to confirm the formula SiO_2 for silica, as the formula SnO_2 was indubitable. Although **stannic fluoride**, SnF_4 , is almost unknown in the free state, its corresponding double salts are very easily formed by the action of hydrofluoric acid on alkaline solutions of stannic oxide; thus, for example, a crystalline salt of the composition $\text{SnK}_2\text{F}_6, \text{H}_2\text{O}$ is obtained by dissolving stannic oxide in potassium hydroxide and then adding hydrofluoric acid to the solution. The barium salt, $\text{SnBaF}_6, 3\text{H}_2\text{O}$, like its corresponding silicofluoride, is sparingly soluble. The more soluble salt of strontium, $\text{SnSrF}_6, 2\text{H}_2\text{O}$, crystallises very well, and is therefore more important for the purposes of research; it is isomorphous with the corresponding salt of silicon (and titanium); the magnesium salt contains $6\text{H}_2\text{O}$.

Stannic sulphide, SnS_2 , is formed, as a yellow precipitate, by the action of sulphuretted hydrogen on acid solutions of stannic salts; it is easily soluble in ammonium and potassium sulphides, because it has an acid character, and then forms thioannates (see Chap. XX.). In an anhydrous state it has the form of brilliant golden yellow plates, which may be obtained by heating a mixture of finely divided tin, sulphur, and sal-ammoniac for a considerable time. It is sometimes used in this form under the name of mosaic gold, as a cheap substitute for gold-leaf in gilding wooden articles. On ignition it parts with a portion of its sulphur, and is converted into stannous sulphide, SnS . It is soluble in caustic alkalis. Hydrochloric acid does not dissolve the anhydrous crystalline compound, but the precipitated powdery sulphide is soluble in boiling strong hydrochloric acid, with the evolution of hydrogen sulphide.

other metals and many metalloids, tin gives a peroxide form of combination or **perstannic oxide**. This substance was obtained by Spring (1889) in the form of hydrate, $\text{H}_2\text{Sn}_2\text{O}_7 = 2(\text{SnO}_3)\text{H}_2\text{O}$, by mixing a solution of SnCl_2 , containing an excess of HCl , with freshly prepared peroxide of barium. A cloudy liquid is then obtained, and after being subjected to dialysis this leaves a gelatinous mass which on drying is found to have the composition $\text{Sn}_2\text{H}_2\text{O}_7$. Above 100° this substance gives off oxygen and leaves SnO_2 . It is evident that SnO_3 bears the same relation to SnO_2 as H_2O_2 to H_2O or ZnO_2 to ZnO , &c.

Tin occupies the same position amongst the analogues of silicon as cadmium and indium amongst the analogues of magnesium and aluminium respectively, and as in each of these cases the heavier analogues with a high atomic weight and a special combination of properties—namely, mercury and thallium—are known, so also for silicon we have **lead** ($\text{Pb} = 207$) as the heaviest analogue, with a series of both kindred and special properties. The higher type, PbX_4 —for instance, PbO_2 and PbCl_4 —is in a chemical sense far less stable than the lower type, PbX_2 , PbO , PbCl_2 &c. The ordinary compounds of lead correspond with the latter, and in addition to this, PbO , although not particularly energetic, is still a decided base easily forming basic salts, $\text{PbX}_2(\text{PbO})_n$. Although the compounds PbX_4 are unstable, they offer many points of analogy with the corresponding compounds of tin, SnO_2 ; this is seen, for instance, from the fact that PbO_2 is a feeble acid, giving the salt PbK_2O_3 , that PbCl_4 is a liquid like SnCl_4 which is not affected by sulphuric acid, and that PbF_4 gives double salts, like SnF_4 or SiF_4 (Brauner, 1894. See Chapter II., note 49a); $\text{Pb}(\text{C}_2\text{H}_5)_4$ also resembles $\text{Sn}(\text{C}_2\text{H}_5)_4$, &c. All this shows that lead is a true analogue of tin, as Hg is of cadmium.^{41a}

Lead is found in nature in considerable masses, in the form of **galena**, i.e., lead sulphide, PbS .⁴² The specific gravity of galena is 7.58, and its colour grey; it crystallises in the regular system, and has a fine metallic lustre. Both the native and artificial sulphides are insoluble in acids (hydrogen sulphide gives a black precipitate with the salts PbX_2).^{42a} When heated, lead melts, and in the open air is either

^{41a} Although the analogy between Sn and Pb has long been generally recognised from the resemblance between the two metals, from a chemical point of view it has only been demonstrated by means of the periodic law.

⁴² Mixed ores of copper compounds, together with PbS and ZnS , are frequently found in the most ancient primary rocks. As the separation of the metals themselves is difficult, the ores are separated by a method of selection or mechanical sorting. Such mixed ores occur in Russia, in many parts of the Caucasus, and in the Donetz district (at Nagolchik).

^{42a} Lead sulphide in the presence of zinc and hydrochloric acid is completely reduced to metallic lead, all the sulphur being given off as hydrogen sulphide.

totally or partially transformed into white lead sulphate, PbSO_4 , as it also is by many oxidising agents (hydrogen peroxide, potassium nitrate). Lead sulphate is also insoluble in water,⁴³ and lead is but rarely met with in this form in nature. The chromates, vanadates, phosphates, and similar salts of lead are also somewhat rare. The carbonate, PbCO_3 , is sometimes found in large masses, especially in the Altai region. Lead sulphide is often worked for extracting the silver which it contains; and as the lead itself also finds manifold industrial applications, this work is carried out on an exceedingly large scale. Many methods are employed. Sometimes the lead sulphide is decomposed by heating it with cast iron. The iron takes up the sulphur from the lead and forms readily fusible iron sulphide, which does not mix with the heavier reduced lead. But another process is more frequently used: the lead ore (it must be clean, that is, free from earthy matter, which may easily be removed by washing) is heated in a reverberatory furnace to a moderate temperature with a free access of air. During this operation part of the lead sulphide oxidises and forms lead sulphate, PbSO_4 , and lead oxide. When the oxidation of part of the lead has been attained, it is necessary to shut off the air supply and raise the temperature, the oxidised compounds of the lead then entering into reaction with the remaining lead sulphide, with formation of sulphurous anhydride and metallic lead. At first, from $\text{PbS} + \text{O}_3$, $\text{PbO} + \text{SO}_2$ are formed, and also from $\text{PbS} + \text{O}_4$ lead sulphate PbSO_4 ; then PbO and PbSO_4 react with the remaining PbS , according to the equations: $2\text{PbO} + \text{PbS} = 3\text{Pb} + \text{SO}_2$ and $\text{PbSO}_4 + \text{PbS} = 2\text{Pb} + 2\text{SO}_2$.⁴⁴

The appearance of lead is well known; its specific gravity is 11.3; the bluish colour and metallic lustre of freshly cut lead quickly

⁴³ Lead sulphate, PbSO_4 , occurs in nature (*anglesite*) in transparent brilliant crystals which are isomorphous with barium sulphate, and have a specific gravity of 6.3. The same salt is formed on mixing sulphuric acid or its soluble salts with solutions of lead salts, as a heavy white precipitate, which is insoluble in water and acids, but dissolves in a solution of ammonium tartrate in the presence of an excess of ammonia. This test serves to distinguish this salt from the similar ones of strontium and barium.

⁴⁴ According to J. B. Hannay (1894) the last-named decomposition ($\text{PbS} + \text{PbSO}_4 = 2\text{Pb} + 2\text{SO}_2$) is really much more complicated, and in fact a portion of the PbS is dissolved in the Pb , forming a slag containing PbO , PbS , and PbSO_4 , whilst a portion of the lead *volatilises* with the SO_2 in the form of a compound PbS_2O_2 , which is also formed in other cases, but has not yet been thoroughly studied.

Besides these methods for extracting lead from PbS in its ores, roasting (the removal of the S in the form of SO_2) and smelting with charcoal with a blast in the same manner as in the manufacture of pig iron (Chap. XXII.) are also employed.

As lead is easily reduced from its ores, and the ore itself has a metallic appearance, it is not surprising that it was known to the ancients, and that its properties were familiar to the alchemists, who called it 'Saturn.' Hence metallic lead, reduced from its salts in solution by zinc, having the appearance of a tree-like mass of crystals, is called 'arbor Saturni,' &c.

disappear when it is exposed to the air, because it becomes coated with a layer—although a very thin one—of oxide and salts formed by the moisture and acids in the atmosphere. It melts at 320° and crystallises in octahedra on cooling. Its softness is apparent from the flexibility of lead pipes and sheets, and also from the fact that it may be cut with a knife, and also that it leaves a grey streak when rubbed on paper. On account of its being so soft, lead naturally cannot be applied in many cases where most metals may be used; but, on the other hand, it is a metal which is not easily changed by chemical reagents, and as it is capable of being soldered and drawn into sheets, &c., lead is most valuable for many other technical uses. Lead pipes are used for conveying water⁴⁵ and many other liquids, and sheet lead is used for lining all kinds of vessels containing liquids (acids, for instance) which act on other metals. This particularly refers to sulphuric and hydrochloric acids, because at ordinary temperatures these do not act on lead, and if they form lead sulphate, PbSO_4 , and chloride, PbCl_2 , these salts, being insoluble in water and in acids, cover the lead and protect it from further corrosion.⁴⁶ All soluble preparations of lead are poisonous. At a white heat lead may be partially distilled; the vapours oxidise and burn. Lead may also be easily oxidised at low temperatures. Lead only decomposes water at a white heat, and does not liberate hydrogen from acids, with the exception only of very strong hydrochloric acid, and this only when boiling. Sulphuric acid diluted with water does not act on it, or only acts very feebly at the surface; but strong sulphuric acid, when heated, is decomposed by it, with the evolution of sulphurous anhydride. The best solvent for lead is nitric acid, which transforms it into a soluble salt, $\text{Pb}(\text{NO}_3)_2$.

⁴⁵ Freshly laid new lead pipes contaminate the water with a certain amount of lead salts, arising from the presence of oxygen, carbonic acid, &c., in the water. But the lead pipes under the action of running water soon become coated with a film of salts—lead sulphate, carbonate, chloride, &c.—which are insoluble in water, and the pipes then become harmless.

⁴⁶ Lead is used in the arts, and, owing to its considerable density, it is cast, mixed with small quantities of other metals, into shot. A considerable amount is employed (together with mercury) in extracting gold and silver from poor ores, and in the manufacture of chemical reagents, and especially of lead chromate. *Lead chromate*, PbCrO_4 , is distinguished for its brilliant yellow colour, owing to which it is employed in considerable quantities as a dye, mainly for dyeing cotton tissues yellow. It is formed on the tissue itself, by causing a soluble salt of lead to react on potassium chromate. Lead chromate is met with in nature as 'red lead ore.' It is insoluble in water and acetic acid, but dissolves in aqueous potash. So-called pewter vessels often consist of an alloy of 5 parts of tin and 1 of lead, and solder is composed of 1 to 2 parts of tin with $\frac{1}{2}$ part of lead. Amongst the alloys of lead and tin, the alloy PbSn_3 stands out from the rest (according to Kupfer and Rydberg), since the temperature remains constant at 187° when an alloy of this composition solidifies. All the other alloys have a higher melting-point. It is evident that this is the eutectic point (Chap. I., note 58).

Although acids thus have directly but little effect on lead, and this is one of its most important practical properties, yet when air has free access, lead (like copper) **very easily reacts with many acids**, even with those which are comparatively feeble. The action of acetic acid on lead is particularly striking and is often applied in practice. If lead is plunged into acetic acid it does not change at all and does not pass into solution, but if part of the lead is immersed in the acid, while the other part remains in contact with the air, or if lead is merely covered with a thin layer of acetic acid in such a way that the air is practically in contact with the metal, then it unites with the oxygen of the air to form oxide, which combines with the acetic acid and forms lead acetate, soluble in water. Not only is the normal lead acetate formed, but also basic salts.⁴⁷

When oxidising in the presence of air,⁴⁸ when heated or in the presence of an acid at the ordinary temperature, lead forms compounds of the type PbX_2 . **Lead oxide**, PbO , is known industrially as **litharge** or **silberglätte** (this name is due to the fact that silver is extracted from the lead ores of this kind) and **massicot**. If the lead is oxidised in air at a high temperature, the oxide which is formed fuses, and on cooling is easily obtained in fused masses which split up into scales of a yellowish-

⁴⁷ The normal lead acetate, known in trade as **sugar of lead**, owing to its having a sweetish taste, has the formula $Pb(C_2H_3O_2)_4 \cdot 3H_2O$. This salt only crystallises from acid solutions. It is capable of dissolving a further quantity of lead oxide or of metallic lead in the presence of air. A basic salt of the composition $Pb(C_2H_3O_2)_2 \cdot PbH_2O_2$ is then formed which is soluble in water and alcohol. As in this salt the number of atoms is even and the same as in the hydrate of acetic acid, $C_2H_4O_2 \cdot H_2O = C_2H_3(OH)_3$, it may be represented as this hydrate in which two of hydrogen are replaced by lead—that is, as $C_2H_3(OH)(O_2Pb)$. This basic salt is used in medicine for bandaging wounds (lead salve), &c., and also in the manufacture of white lead. Other basic acetates of lead, containing a still greater amount of lead oxide, are known. According to the above representation of the composition of the preceding lead acetate, a basic salt of the composition $(C_2H_3)_2(O_2Pb)_3$ would also be possible, but what appear to be still more basic salts are known. As the character of a salt also depends on the property of the base from which it is formed, it would seem that lead forms a hydroxide of the composition $HOPbOH$, containing two water residues, one or both of which may be replaced by the acid residues. If both water residues are replaced, a normal salt, $XPbX$, is obtained, whilst if only one is replaced a basic salt, $XPbOH$, is formed. But lead gives not only this normal hydroxide, but also polyhydroxides, $Pb(OH)_2 \cdot PbO$, and if we may imagine that in these polyhydroxides there is a substitution of both the water residues by acid residues, then the power of lead to form basic salts is explained by the properties of the base which enters into their composition.

⁴⁸ Few compounds are known of the lower type PbX , and still fewer of the intermediate type PbX_3 . To the first type belongs the so-called lead suboxide, Pb_2O , obtained by the ignition of lead oxalate, C_2PbO_4 , without access of air. It is a black powder, which easily breaks up under the action of acids, and even by the simple action of heat, into metallic lead and lead oxide. This is the character of all suboxides. It is difficult to regard them as independent salt-forming oxides, because they have not the colour of salts. Such is red lead (see further on).

grey colour, having a specific gravity of 9.3; in this form it bears the name of litharge. Litharge is principally used for making lead salts, for the extraction of metallic lead, and also for the preparation of drying oils—for instance, from linseed oil.⁴⁹ When oxidised carefully and slightly heated, lead forms a powdery (not fused) oxide known under the name of **massicot**. It is best prepared in the laboratory by heating lead nitrate, or lead hydroxide. It has a yellow colour, and when moistened with water does not attract the carbonic acid of the air so easily as litharge does, owing to the superficial formation of dioxide on which acids do not act. In any case lead oxide is comparatively easily soluble in nitric and acetic acids. It is but slightly soluble in water, but communicates an alkaline reaction to it, since it forms the hydroxide. This **hydroxide** is obtained in the shape of a white precipitate by the action of a small quantity of an alkali hydroxide on a solution of a lead salt. An excess of alkali dissolves the hydroxide separated, which fact demonstrates the comparatively indistinct basic properties of lead oxide. The normal lead hydroxide, which should have the composition $\text{Pb}(\text{OH})_2$, is unknown in a separate state, but it is known in polymeric combination with lead oxide as $\text{Pb}(\text{OH})_2, 2\text{PbO}$ or $\text{Pb}_3\text{O}_2(\text{OH})_2$. The latter is obtained in the form of brilliant white octahedral crystals when basic lead acetate is mixed with ammonia and gently heated. It absorbs the carbonic anhydride of the air. When an alkaline solution of the hydroxide is boiled, it deposits lead oxide in the form of a crystalline powder.

Lead oxide forms but few soluble salts—for instance, the nitrate and the acetate. The majority of its salts (sulphate, PbSO_4 ; carbonate, PbCO_3 ; iodide, PbI_2 , &c.) are insoluble in water. These salts are colourless or pale yellow if the acid is colourless. In lead oxide the **faculty of forming basic salts**, $\text{PbX}_2, n\text{PbO}$ or $\text{PbX}_2, n\text{PbH}_2\text{O}_2$, is strongly developed. A similar property was observed in magnesium and also in the salts of mercury, but lead oxide forms basic salts with still greater facility, although double salts are in this case more rarely formed.⁵⁰

⁴⁹ In the boiling of drying oils (linseed, poppy seed, &c.), the lead oxide passes partially into solution, forming a saponified compound capable of attracting oxygen and solidifying to a tarlike mass, which forms the oil paint. Perhaps, however, glycerine has some action in the process. Ossowetsky, by saturating drying oil with the salts of certain metals, obtained oil colours of great durability.

A mixture of very finely divided litharge with glycerine (50 grams of litharge to 5 e.e. of anhydrous glycerine) forms a very quick (two minutes) setting cement, which is insoluble in water and oils, and is very useful in setting up chemical apparatus.

⁵⁰ It is very instructive to observe that lead easily forms not only basic salts, but also salts containing several acid groups. Thus, for example, lead carbonate forms compounds with lead chloride and sulphate. The first compound known as **corneous lead**

Amongst the soluble lead salts, that best known and most often applied in practical chemistry is **lead nitrate**, $\text{Pb}(\text{NO}_3)_2$, obtained directly by dissolving lead or its oxide in nitric acid. It crystallises in octahedra, and has a specific gravity of 4.5. When a solution of this salt is boiled with litharge, the basic salt, having a composition $\text{Pb}(\text{OH})(\text{NO}_3)$, is formed in crystalline needles, sparingly soluble in cold water but easily dissolved in hot water, and therefore much resembling lead chloride. When the nitrate is heated, either lead oxide is obtained or else the oxide in combination with peroxide. **Lead chloride**, PbCl_2 , is precipitated from the soluble salts of lead when strong solutions are treated with hydrochloric acid or a metallic chloride. It is soluble in considerable quantities in hot water, and therefore, if the solutions be dilute or hot, the precipitation of lead chloride does not occur, and if the solution be cooled, the salt separates in brilliant prismatic crystals. It easily fuses when heated (like silver chloride), but is insoluble in ammonia. This salt is sometimes met with in nature, and when heated in air is capable of exchanging half its chlorine for oxygen, forming the basic salt or lead oxychloride, $\text{PbCl}_2, \text{PbO}$, which may also be obtained by fusing PbCl_2 and PbO together. The reaction of lead chloride with water vapour leads to the same conclusion, showing the feeble basic character of oxide of lead, $2\text{PbCl}_2 + \text{H}_2\text{O} = \text{PbCl}_2, \text{PbO} + 2\text{HCl}$. When ammonia is added to an aqueous solution of lead chloride a white precipitate is formed, which parts with water on being heated, and has the composition $\text{Pb}(\text{OH})\text{Cl}, \text{PbO}$. This compound is also formed by the action of metallic chlorides on other soluble basic salts of lead.⁵¹

or *phosgenite*, has the composition $\text{PbCO}_3, \text{PbCl}_2$; it occurs in nature in bright cubic crystals, and is prepared artificially by simply boiling lead chloride with lead carbonate. A similar compound of normal salts, $\text{PbSO}_4, \text{PbCO}_3$, occurs in nature as **lanarkite** in monoclinic crystals. **Leadhillite** has the composition $\text{PbSO}_4, 3\text{PbCO}_3$, and also occurs in yellowish, monoclinic, tabular crystals. In describing silica we carefully developed the conception of polymerisation, which it is *also indispensable to recognise in the composition of many other oxides*. Thus it may be supposed that PbO and PbO_2 are polymerised compounds similar to SiO_2 —i.e., that the composition of lead peroxide will be Pb_nO_{2n} and that of the oxide Pb_nO_n . This consideration respecting the complexity of lead oxide could have no real significance, and could not be accepted, were it not for the existence of the above-mentioned basic and mixed salts. The oxide apparently corresponds with the composition Pb_nX_{2n} , and since, according to this representation, the number of X's in the salts of lead is considerable, it is obvious that they may be diverse. When a part of these X's is replaced by the water residue (OH) or by oxygen, $\text{X}_2 = \text{O}$, and the other parts by an acid residue X, basic salts are obtained; but if a part of the X's is replaced by acid residues of one kind, and the other part by acid residues of another kind, then those mixed salts about which we are now speaking are formed. The theory of the polymerisation of oxides introduced by me in the first edition of this work (1869) is now beginning to be generally accepted, and has been applied by many in investigating the hydrates and basic salts of different metals.

⁵¹ A similar basic salt having a white colour, and therefore used as a substitute for

Lead carbonate, or **white lead**, is the most extensively used basic lead salt. It has the valuable faculty of 'covering,' to a greater extent than appertains to other substances. This faculty consists in the fact that a small quantity of white lead mixed with oil spreads uniformly, and if such a mixture is spread over a surface (for instance, of wood or metal), light does not penetrate through, so that the grain of the wood remains invisible.⁵² White lead, or **basic lead carbonate**, after being dried at 120° , has the composition $\text{Pb}(\text{OH})_2, 2\text{PbCO}_3$.⁵³ It may be obtained by adding a solution of sodium carbonate to a solution of one of the basic salts of lead—for instance, the basic acetate—and likewise by treating this latter with carbonic acid. For this purpose the solution of basic acetate is poured into the vessel *f*; it is prepared in the vat A, containing litharge, into which the pump P delivers the solution of the acetate, which remains after the action of carbonic anhydride on the basic salt. In A a basic salt is formed having a composition approaching to $\text{Pb}_4(\text{OH})_6(\text{C}_2\text{H}_3\text{O}_2)_2$; carbonic anhydride, 2CO_2 , is passed through this solution and precipitates white lead, $\text{Pb}_2(\text{OH})_2(\text{CO}_3)_2$, while normal lead acetate, $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$, remains in the solution, and is pumped back into the vat A containing lead

white lead, is also obtained by mixing a solution of basic lead acetate with a solution of lead chloride. Its formation is expressed by the equation: $2\text{PbX}(\text{OH}), \text{PbO} + \text{PbCl}_2 = 2\text{Pb}(\text{OH})\text{Cl}, \text{PbO} + \text{PbX}_2$. Similar basic compounds of lead are met with in nature—for instance, *mendipite*, $\text{PbCl}_2, 2\text{PbO}$, which appears in brilliant yellowish-white masses. The ignition of red lead with sal-ammoniac results in similar polybasic compounds of lead chloride, forming *Cassel's* or *mineral yellow* of the composition $\text{PbCl}_2, n\text{PbO}$. **Lead iodide**, PbI_2 , is still less soluble than the chloride, and is therefore obtained by mixing potassium iodide with a solution of a lead salt. It separates as a yellow powder, which may be dissolved in boiling water, and on cooling separates in very brilliant crystalline scales of a golden-yellow colour. The salts PbBr_2 , PbF_2 , $\text{Pb}(\text{CN})_2$, $\text{Pb}_2\text{Fe}(\text{CN})_6$ are also insoluble in water, and form white precipitates

⁵² It is remarkable that a peculiar kind of attraction exists between boiled linseed oil and white lead, as is seen from the following experiments. White lead is triturated in water. Although it is heavier than water, it remains in suspension in it for some time and is thoroughly moistened by it, so that the trituration may be made perfect; boiled linseed oil is then added, and shaken up with it. A mixture of the oil and white lead is then found to settle at the bottom of the vessel. Although the oil is lighter than the water it does not float on the top, but is retained by the white lead and sinks with it under the water. There is not, however, any more perfect combination nor even any solution. If the resultant mass be then treated with ether or any other liquid capable of dissolving the oil, the latter passes into solution and leaves the white lead unaltered.

⁵³ White lead may be regarded as a salt corresponding with the normal hydrate of carbonic acid, $\text{C}(\text{OH})_2$, in which three-quarters of the hydrogen is replaced by lead. A salt is also known in which all the hydrogen of this hydrate of carbonic acid is replaced by lead—namely, the salt of the composition CO_3Pb_2 . This salt is obtained as a white crystalline substance by the action of water and carbonic acid on lead. The normal salt, PbCO_3 , occurs in nature under the name of white lead ore (sp. gr. 6.47), in crystals isomorphous with aragonite, and is formed as a heavy white precipitate by the double decomposition of lead nitrate with sodium carbonate.

oxide, where the normal salt is again (on being agitated) converted into the basic salt. This is run into the vessel E, and thence into *f*. Into the latter, carbonic anhydride is delivered from the generator D, and forms a precipitate of white lead.^{53a}

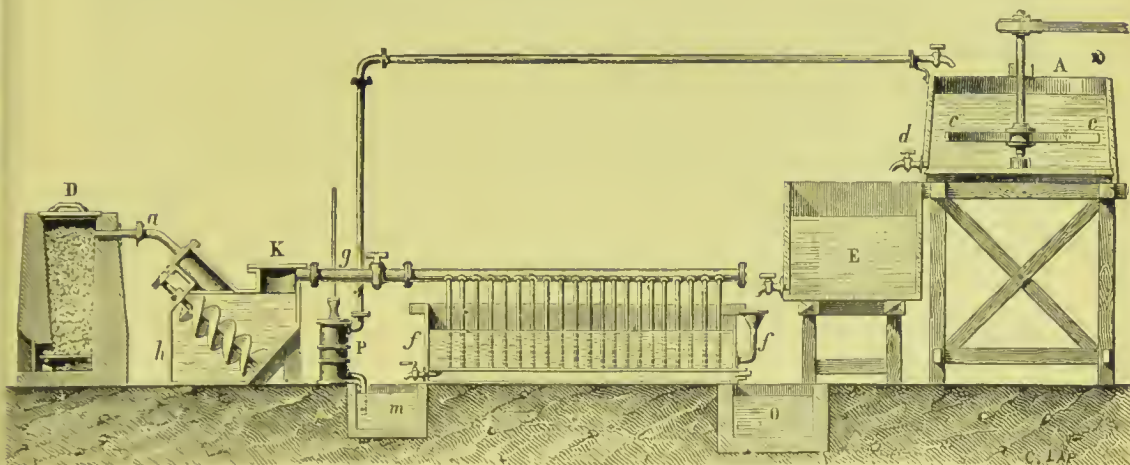


FIG. 93.—Apparatus for the manufacture of white lead.

In order to mark the transition from lead oxide, PbO , into lead dioxide PbO_2 (plumbic anhydride), it is necessary to direct our attention to the intermediate oxide, or **red lead**, Pb_3O_4 .⁵⁴ In the arts it is used in considerable quantities, because it forms a very durable yellowish-red paint used for colouring the resins (shellac, colophony, &c.) composing sealing-wax. It also forms a very good cheap oil paint, used especially for painting metals, more particularly because drying oils—for instance, hempseed and linseed oils—quickly dry with red lead and with lead salts. Red lead is prepared by slightly heating

^{53a} One of the many methods by which white lead is prepared consists in mixing massicot with acetic acid or sugar of lead, and leaving the mixture exposed to air (and re-mixing from time to time) containing carbonic acid, which is absorbed from the surface by the basic salt formed. After repeated mixings (with the addition of water), the entire mass is converted into white lead, which is thus obtained very finely divided.

⁵⁴ If lead hydroxide is dissolved in potash and sodium hypochlorite is added to the solution, the oxygen of the latter acts on the dissolved lead oxide, and partially converts it into dioxide, so that the so-called **lead sesquioxide** is obtained; its empirical formula is Pb_2O_3 . Probably it is nothing but lead plumbate—i.e., hydroxide of dioxide of lead, $\text{PbO}(\text{OH})_2$, in which two atoms of hydrogen are replaced by lead, $\text{PbO}(\text{O}_2\text{Pb})$. The brown compound precipitated by the action of dilute acids—for example, nitric—splits up, even at the ordinary temperature, into insoluble lead dioxide and a solution of a lead salt. This compound evolves oxygen when it is heated. It dissolves in hydrochloric acid, forming a yellow liquid, which probably contains compounds of the composition PbCl_2 and PbCl ; but even at the ordinary temperature the latter soon loses the excess of chlorine, and then only lead chloride, PbCl_2 , remains. In order to see the relation between red lead, Pb_3O_4 , and lead sesquioxide, it must be observed that they only differ by an extra quantity of lead oxide—that is, red lead is a basic salt of the preceding compound.

massicot in air, for which purpose two-storied stoves are used. In the lower story the lead is turned into massicot, and in the higher one, having the lower temperature (about 300°), the massicot is transformed into red lead. Frémy and others showed the instability of red lead prepared by various methods, and its decomposition by acids, with formation of lead dioxide, which is insoluble in acids, and a solution of the salts of lead oxide. The artificial production (synthesis) of red lead by double decomposition was most important. For this purpose Frémy mixed an alkaline solution of **potassium plumbate**, K_2PbO_3 (prepared by dissolving the dioxide in fused potash),^{54a} with an alkaline solution of lead oxide. In this way a yellow precipitate of minium hydrate is formed, which, when slightly heated, loses water and turns into bright red anhydrous minium, Pb_3O_4 .

Minium is the first and most ordinary means of producing **lead dioxide**, or plumbic anhydride, PbO_2 ,⁵⁵ because when red lead is treated with dilute nitric acid it gives up lead oxide, and leaves PbO_2 on which dilute nitric acid does not act. The composition of minium is Pb_3O_4 , and therefore the action of nitric acid on it is expressed by the equation : $Pb_3O_4 + 4HNO_3 = PbO_2 + 2Pb(NO_3)_2 + 2H_2O$. The dioxide may also be obtained by treating lead hydroxide suspended in

^{54a} Frémy obtained **potassium plumbate** in the following manner. Pure lead dioxide is placed in a silver crucible, and a strong solution of pure caustic potash is poured over it. The mixture is heated and small quantities are removed from time to time for testing, which consists in dissolving in a small quantity of water and decomposing the resultant solution with nitric acid. There is a certain moment during the heating when a considerable amount of insoluble lead dioxide is precipitated on the addition of the nitric acid; the solution then contains the salt in question, and the heating must be stopped, and a small amount of water added to dissolve the potassium plumbate formed. On cooling, the salt separates in somewhat large crystals, which have the same composition as the stannate—that is, $PbO(KO)_2 \cdot 3H_2O$.

⁵⁵ Lead dioxide is often called **lead peroxide**; but this name leads to error, because PbO_2 does not show the properties of true peroxides, like those of hydrogen or barium, but is endowed with acid properties—that is, it is able to form true salts with bases, which is not the case with true peroxides. Lead dioxide is a normal salt-forming compound of lead, as Bi_2O_5 is for bismuth, CeO_2 for cerium, and TcO_3 for tellurium, &c. They all evolve chlorine when treated with hydrochloric acid, whilst true peroxides form hydrogen peroxide. The true lead peroxide, if it were obtained, would probably have the composition Pb_2O_5 , or, in combination with peroxide of hydrogen, $H_2Pb_2O_7 = H_2O_2 + Pb_2O_5$, judging from the peroxides corresponding with sulphuric, chromic, and other acids, which we shall afterwards consider.

As a proof of the fact that the form PbO_2 , or PbX_4 , is the highest normal form of any combination of lead, it is most important to remark that it might be expected that the action of lead chloride, $PbCl_2$, on zinc-ethyl, $ZnEt_2$, would result in the formation of zinc chloride, $ZnCl_2$, and lead-ethyl, $PbEt_2$, but that in reality the reaction proceeds otherwise. Half of the lead is set free, and lead tetrethyl, $PbEt_4$, is formed as a colourless liquid, boiling at about 200° (Butleroff, Frankland, Buckton, Cahours, and others). The type PbX_4 is not only expressed in $PbEt_4$ and PbO_2 , but also in PbF_4 , obtained by Brauner (Chap. XI., note 49a).

water with a stream of chlorine. Under these conditions the chlorine takes up the hydrogen from the water, and the oxygen passes over to the lead oxide.⁵⁶ When a strong solution of lead nitrate is decomposed by the electric current, the appearance of crystalline lead dioxide is also observed upon the positive pole; it is also found in nature in the form of a black crystalline substance having a specific gravity of 9.4. When artificially produced it is a fine dark powder, resisting the action of acids, but nevertheless when treated with strong sulphuric acid it evolves oxygen and forms lead sulphate, and with hydrochloric acid it evolves chlorine. The oxidising property of lead dioxide depends of course on the facility of its transition into the more stable lead oxide, which is easily understood from the whole history of lead compounds. In the presence of alkalis it transforms chromium oxide into chromic acid, lead chromate, PbCrO_4 , being formed and remaining in solution, on account of its being soluble in caustic alkalis. The oxidising action of lead dioxide on sulphurous anhydride is most striking, as it immediately absorbs it, with formation of lead sulphate. This is accompanied by a change of colour and development of heat, $\text{PbO}_2 + \text{SO}_2 = \text{PbSO}_4$. When triturated with sulphur the mixture explodes, the sulphur burning at the expense of the oxygen of the lead dioxide. **Tetrachloride of lead**, PbCl_4 , belongs to the same class of lead compounds as PbO_2 . This chloride is formed by the action of strong hydrochloric acid upon PbO_2 , or, in the cold, by passing a stream of chlorine through water containing PbCl_2 in suspension. The resultant yellow solution gives off chlorine when heated. With a solution of sal-ammoniac (Nikolukine, 1885) it gives a precipitate of a double salt, $(\text{NH}_4)_2\text{PbCl}_6$ (very slightly soluble in a solution of sal-ammoniac), which when treated with strong sulphuric acid (Friedrich, 1890) gives PbCl_4 as a yellow liquid of sp. gr. 3.18, which solidifies at -18° , and when heated gives $\text{PbCl}_2 + \text{Cl}_2$. It is not acted upon by H_2SO_4 , like SnCl_4 . Tetrafluoride of lead (Brauner) belongs to the same class of compounds; it easily forms double salts and decomposes with evolution of fluorine (Chap. II., note 49a).^{56a}

⁵⁶ According to Carnelley and Walker, the hydrate $(\text{PbO}_2)_3 \cdot \text{H}_2\text{O}$ is then formed; it loses water at 230° . The anhydrous dioxide remains unchanged up to 280° , and is then converted into the sesquioxide, Pb_2O_3 , which again loses oxygen at about 400° , and forms red lead, Pb_3O_4 . Red lead also loses oxygen at about 550° , forming lead oxide, PbO , which fuses without change at about 600° , and remains constant as far as the limit of the observations made (about 800°).

The best method for preparing pure lead dioxide consists in mixing a hot solution of lead chloride with a solution of bleaching powder (Fehrman). Under the action of a galvanic current, lead salts give not only PbO_2 , but also its compounds; for instance, $\text{Pb}(\text{SO}_4)_2$, which may be regarded as a salt of persulphuric acid and PbO .

^{56a} The plumbates of Ca and other similar metals, mentioned in Chap. III., note 7, also belong to the form PbX_4 .

In the second and third groups it was observed that the elements were more basic in the even than in the uneven series. It is sufficient to remember calcium, strontium, and barium in the even, and magnesium, zinc, and cadmium in the uneven series. In addition to this, in the even series, as the atomic weight increases, in the same type of oxidation the basic properties increase (the acid properties decrease); for example, in the second group, calcium, strontium, barium. The same also appears in the fourth and all the following groups. In the even series of the fourth group, titanium, zirconium, cerium, and thorium are found. All their highest oxides, RO_2 , even the lightest—titanic oxide, TiO_2 —have more highly developed basic properties than silica, SiO_2 , and in addition to this the basic properties are more distinctly seen in zirconium dioxide, ZrO_2 , than in titanic oxide, TiO_2 , although the acid property of combining with bases still remains. In the heaviest oxides, cerium dioxide, CeO_2 , and thorium dioxide, ThO_2 , no acid properties are observed, these being both purely basic oxides. This higher oxide of cerium has already been described in the preceding chapter, and as titanium and zirconium are rather rare in nature, have but little practical application, and do not present any new forms of combination, it is inadvisable to dwell on them in this treatise.

Titanium is found in nature in the form of its anhydride or oxide, TiO_2 , mixed with silicon in many silicious minerals (even in clay and bauxite), but the oxide is also found separately in the form of semi-metallic **rutile** (sp. gr. 4·2). Another titanic mineral is found as a mixture in other ores, known as **titanic iron ore** (in the Thuensky mountains of the southern Ural; it is known as *thuenite*), FeTiO_3 . This is a salt of ferrous oxide and titanic anhydride. It crystallises in the rhombohedral system, has a metallic lustre, a grey colour, and the sp. gr. 4·5. The third mineral in which titanium is found in considerable quantities in nature is *sphene* or *titanite*, $\text{CaTiSiO}_5 = \text{CaO}, \text{SiO}_2, \text{TiO}_2$, sp. gr. 3·5, colour yellow, green, or the like, crystallises in tablets. The fourth, but rare, titanic mineral is *perovskite*, calcium titanate, CaTiO_3 ; it forms blackish-grey or brown cubic crystals, sp. gr. 4·02, and occurs in the Ural and other localities. It may be prepared artificially by fusing sphene in an atmosphere of water vapour and carbonic anhydride. At the end of the last century Klaproth showed the distinction between titanic compounds and all others then known.⁵⁷

⁵⁷ The compounds of titanium are generally obtained from rutile; the finely ground ore is fused with a considerable amount of acid potassium sulphate, until the titanic anhydride, as a feeble base, passes into solution. After cooling, the resultant mass is ground up, dissolved in cold water, and treated with ammonium hydrosulphide; a black precipitate then separates out from the solution. This precipitate contains TiO_2 (as

The comparatively rare element **zirconium**, $Zr=90$, is very similar to titanium, and has a more basic character. It is rarer in nature

hydrate) and various metallic sulphides—for example, iron sulphide. It is first washed with water and then with a solution of sulphurous anhydride until it becomes colourless. This is due to the iron sulphide, which is contained in the precipitate, and renders it black, being converted into dithionate by the action of the sulphurous acid. The titanic acid left behind is nearly pure. The considerable volatility of titanium chloride may also be taken advantage of in preparing the compounds of titanium from rutile. It is formed by strongly heating a mixture of rutile and charcoal in dry chlorine; the distillate then contains **titanium chloride**, $TiCl_4$. It may be easily purified, owing to its having a constant boiling-point of 136° . Its specific gravity is 1.76; it is a colourless liquid, which fumes in the air, and is perfectly soluble in water if it is not heated. When hot water acts on titanic chloride, a large proportion of titanic acid separates out from the solution and passes into metatitanic acid. A similar decomposition of acid solutions of titanic acid is accomplished whenever they are heated, and especially in the presence of sulphuric acid, just as with metastannic acid, which titanic acid resembles in many respects. On igniting the titanic acid a colourless powder of the anhydride, TiO_2 , is obtained. In this form it is no longer soluble in acids or alkalies, and only fuses in the oxy-hydrogen flame; but, like silica, it dissolves when fused with alkalies or their carbonates; as already mentioned, it dissolves when fused with a considerable excess of acid potassium sulphate—that is, it then reacts as a feeble base. This shows the basic character of titanic anhydride; it has at once, although feebly developed, both basic and acid properties. The fused mass, obtained from titanic anhydride and alkali when treated with water, parts with its alkali, and a residue is obtained of a sparingly soluble poly-titanate, $K_2TiO_3 \cdot nTiO_2$. The hydrate, which is precipitated by ammonia from the solutions obtained by the fusion of TiO_2 with acid potassium sulphate, when dried forms an amorphous mass of the composition $Ti(OH)_4$. But it loses water over sulphuric acid, gradually passing into a hydrate of the composition $TiO(OH)_2$, and when heated it parts with a still larger proportion of water; at 100° the hydrate $Ti_2O_3(OH)_2$ is obtained, and at 300° the anhydride itself. The higher hydrate, $Ti(OH)_4$, is soluble in dilute acid, and the solution may be diluted with water; but on boiling the sulphuric acid solution (though not the solution in hydrochloric acid), all the titanic acid separates in a modified form, which is, however, not only soluble in dilute acids, but even in strong sulphuric acid. This hydrate has the composition $Ti_2O_3(OH)_2$, but shows different properties from those of the hydrate of the same composition described above, so that this modified hydrate is called **metatitanic acid**. It is most important to note the property of the ordinary gelatinous hydrate (that precipitated from acid solutions by ammonia) of dissolving in acids, the more so since silica does not show this property. In this property a transition apparently appears between the cases of common solution (based on a capacity for unstable combination) and the case of the formation of a hydrosol (the solubility of germanium oxide, GeO_2 , perhaps presents another such instance). When heated in hydrogen, TiO_2 gives a sesquioxide, Ti_2O_3 , which forms alums, like Al_2O_3 . If titanium chloride be added drop by drop to a dilute solution of alcohol and hydrogen peroxide, and then ammonia be added to the resultant solution, a yellow precipitate of *titanium trioxide*, $TiO_3 \cdot H_2O$, separates out, as has been shown by Piccini, Weller, Classen, and Levy. This substance apparently belongs to the category of true peroxides.

Titanium chloride absorbs ammonia and forms a compound, $TiCl_4 \cdot 4NH_3$, as a reddish-brown powder which attracts moisture from the air and when ignited forms **titanium nitride**, Ti_3N_4 . Phosphoretted hydrogen, hydrocyanic acid, and many similar compounds are also absorbed by titanium chloride, with the evolution of a considerable amount of heat. Thus, for example, a yellow crystalline powder of the composition $TiCl_4 \cdot 2HCN$ is obtained by passing dry hydrocyanic acid vapour into cold titanium chloride. Metallic titanium, obtained as a grey powder by reducing potassium titanofluoride, K_2TiF_6 (sp. gr. 3.55, K. Hofman, 1893), with iron in a charcoal crucible, combines directly with nitrogen at a red heat. If titanic anhydride be ignited in a stream of ammonia, all the

than titanium, and is found principally in a mineral called *zircon*, $\text{ZrSiO}_4 = \text{ZrO}_2 \cdot \text{SiO}_2$, crystallising in square prisms of sp. gr. 4.5. It has considerable hardness and a characteristic brownish-yellow colour, and is occasionally found in the form of transparent crystals, as a precious stone called *hyacinth*.⁵⁸ Metallic **zirconium** was obtained, by Berzelius

oxygen of the titanic oxide is disengaged, and the compound TiN_2 is formed as a dark violet substance having a copper-red lustre. A compound Ti_3N_4 is also known; it is obtained by igniting the compound Ti_3N_4 in a stream of hydrogen, and is of a golden-yellow colour with a metallic lustre. To this order of compounds belongs also the well-known and chemically historical compound known as **titanium nitrocyanide**; its composition is Ti_5CN_4 . This substance appears as infusible, sometimes well formed, cubic crystals of sp. gr. 4.8, and having a red copper colour and metallic lustre; it is found in blast furnace slag: It is insoluble in acids, but is acted on by chlorine at a red heat, forming titanium chloride. It was at first regarded as metallic titanium; it is formed in the blast furnace at the expense of those cyanogen compounds (potassium cyanide and others) which are always present, and of the titanium compounds which accompany the ores of iron. Wöhler, who investigated this compound, obtained it artificially by heating a mixture of titanic oxide with a small quantity of charcoal, in a stream of nitrogen, and thus proved the direct power for combination between nitrogen and titanium. When fused with caustic potash, all the nitrogen compounds of titanium evolve ammonia and form potassium titanate. Like metals, they are able to reduce many oxides—for example, those of copper—at a red heat. Among the alloys of titanium, the crystalline compound Al_4Ti is remarkable. It is obtained by directly dissolving titanium in fused aluminium; its specific gravity is 3.11. The crystals are very stable, and are only soluble in aqua regia and alkalies.

⁵⁸ The formula ZrO was first given to the basic oxide of zirconium, taking $\text{Zr} = 45$; the present atomic weight, however, is $\text{Zr} = 90.6$, so that the formula of the oxide is now recognised as being ZrO_2 . The reasons for ascribing this formula to the compounds of zirconium are as follows. In the first place, the investigation of the crystalline forms of the zirconofluorides—for example, K_2ZrF_6 , $\text{MgZrF}_6 \cdot 5\text{H}_2\text{O}$ —which proved to be analogous in composition and crystalline form with the corresponding compounds of titanium, tin, and silicon. In the second place, the specific heat of Zr is 0.067, which corresponds with the atomic weight 90. The third and most important reason for doubling the combining weight of zirconium was given by Deville's determination of the vapour density of **zirconium chloride**, ZrCl_4 . This substance is obtained by igniting zirconium oxide mixed with charcoal in a stream of dry chlorine, and is a colourless saline substance which is easily distilled at 440° . Its density referred to air was found to be 8.15, that is, 117 in relation to hydrogen, as it should be according to the molecular formula of this substance above cited. It exhibits, however, in many respect a saline character and that of an acid chloranhydride, for zirconium oxide itself presents very feebly developed acid properties but clearly marked basic properties. Thus zirconium chloride dissolves in water, and on evaporation the solution only partially disengages hydrochloric acid—resembling magnesium chloride, for example. Zirconium was discovered and characterised as an individual element by Klaproth.

Pure compounds of zirconium are generally prepared from zircon, which is finely ground; but as it is very hard it is first heated and thrown into cold water, by which means it is disintegrated. Zircon is decomposed or dissolved when fused with acid potassium sulphate, or still more easily when fused with acid potassium fluoride (a double soluble salt, K_2ZrF_6 , is then formed); however, zirconium compounds are generally prepared from powdered zircon by fusing it with sodium carbonate and then boiling in water. An insoluble white residue is obtained consisting of a compound of the oxides of sodium and zirconium, which is then treated with hydrochloric acid and the solution evaporated to dryness. The silica is thus converted into an insoluble form, and zirconium chloride obtained in solution. Ammonia precipitates **zirconium**

and Troost, by the action of aluminium on potassium zirconofluoride in the same way that silicon is prepared; it forms a crystalline powder, similar in appearance to graphite and antimony, but having a very considerable hardness, not much lustre, and a sp. gr. 4.15. In many respects it resembles silicon; it does not fuse when heated, and even oxidises with difficulty, but liberates hydrogen when fused with potash. When fused with silica it liberates silicon. With carbon in the electric furnace it forms ZrC_2 and with hydrogen it gives ZrH_2 (Winkler); hydrochloric and nitric acids act feebly on it, but aqua regia easily dissolves it. It is distinguished from silicon by the fact that hydrofluoric acid acts on it with great facility, even in the cold and when diluted, whilst this acid does not act on silicon at all.

The very similar element **thorium** ($\text{Th}=232$) was distinguished by Berzelius (1828) from zirconium. It is met with in the very rare *thorite* and *orangeite*, $\text{ThSiO}_4 \cdot 2\text{H}_2\text{O}$ (sp. gr. 4.8), and also in the cerite and gadolinite earths, especially in monazite, which is a phosphate of cerium, CePO_4 , in which a portion of the oxide of cerium is replaced by the oxides of other rare earths, including thorium (see Chap. XVII.; Brauner). The monazite of Carolina contains as much as 4 per cent. of ThO_2 .⁵⁹ Although oxide of thorium resembles the oxides R_2O_3

hydroxide from this solution, as a white gelatinous precipitate, $\text{ZrO}(\text{OH})_2$. When ignited, this hydroxide loses water and in so doing undergoes spontaneous recalescence and leaves a white infusible and exceedingly hard mass of **zirconium oxide**, ZrO_2 , having a specific gravity of 5.4 (in the electric furnace, ZrO_2 fuses and volatilises like SiO_2 —Moissan). Owing to its infusibility, zirconium oxide is used as a substitute for lime and magnesia in the Drummond light. This oxide, in contradistinction to titanium oxide, is soluble, even after prolonged ignition, in hot strong sulphuric acid. The hydroxide is readily soluble in acids. The composition of the salts is ZrX_4 , or ZrOX_2 or $\text{ZrOX}_3 \cdot \text{ZrO}_2$, just as with those of its analogues. But although zirconium oxide forms salts in the same way with acids, it also gives salts with bases. Thus, it liberates carbonic anhydride when fused with sodium carbonate, forming the salts $\text{Zr}(\text{NaO})_4$, $\text{ZrO}(\text{NaO})_2$, &c. Water, however, destroys these salts and extracts the soda.

⁵⁹ ThO_2 is obtained by heating finely powdered thorite with sulphuric acid and precipitating the solution (after treating with H_2S) with alkali. The resultant hydrate, $\text{Th}(\text{OH})_4$, is then dissolved in acid, re-precipitated with oxalic acid, and ignited. The oxide is purified by converting it into sulphate, which is soluble (in an anhydrous form, after heating to 450°) in ice-cold water. The solution, like those of the sulphates of all the 'rare earths,' when heated deposits a portion of its salt in crystals, having the composition $\text{Th}(\text{SO}_4)_2 \cdot 9\text{H}_2\text{O}$. A very pure salt may be obtained by repeating this process several times. In treating monazite, the majority of the cerite earths are separated by taking advantage either of the fact that the precipitated sodium oxalate salt is easily soluble in a solution of the ammonium oxalate salt (like the salts of ytterbium), but is precipitated from solutions strongly acidulated with sulphuric acid (the salt of Yb_2O_3 , then remains in solution) or the double ammonium oxalate is treated with an excess of nitric acid, in which case the thorium salt is precipitated and the accompanying metals remain in solution, or else other more complex methods are employed, based on the fact that the thorium salt of hydrazoic acid, HN_3 , is insoluble. The treatment of thorite, and especially of monazite, is carried out on a large scale for preparing the nitrate, $\text{Th}(\text{NO}_3)_4$ (crystallising with 12 or 6 or $5\text{H}_2\text{O}$) which is used in the mantles of the Auër

of the 'rare earths' (cerite and gadolinite),⁶⁰ and exhibits feebly basic properties, yet it undoubtedly belongs to the oxides RO_2 , not only because of its isomorphism with the compounds of Ti and Zr (Delafontaine, 1863) and the atomic weight of about 232-233 (if the oxide have the composition ThO_2 , of which there can be no doubt), but also from the vapour density of the difficultly volatile chloride ThCl_4 (obtained by heating a mixture of ThO_2 and carbon in a stream of chlorine and also by other methods) and the specific heat of the metal (0.028), obtained by fusing the double salt of KCl and ThCl_4 with sodium and having a sp. gr. of about 11.1, according to Clève, Nilson, and Krüss.⁶¹ The salts of oxide of thorium, ThX_4 , are colourless, give no absorption spectrum, and as salts of a feeble base easily give ThOX_2 .

v. Welsbach incandescent burners. The idea of these burners originally came from Bunsen, who observed that the 'rare earths,' and especially the oxide of erbium, emit a brilliant light when heated. A mixture of ThO_2 with 1 per cent. of CeO_2 is now used for this purpose. The network mantle is soaked in a solution of the nitrates of these metals and calcined. A skeleton of the oxides then remains in the place of the net, and is used for giving an incandescent light in a smokeless flame of a gas or kerosene burner (Bunsen). This gives a most brilliant and also economical light.

⁶⁰ Like the oxides R_2O_3 of the rare metals, oxide of thorium, ThO_2 , in the form of its salts, ThX_4 , gives with alkalis a precipitate of the colourless hydrate, $\text{Th}(\text{OH})_4$. The precipitate given by oxalic acid is insoluble in feeble acids, just as with the cerite oxides, and the double sulphate is also insoluble in a saturated solution of K_2SO_4 . But the precipitate of the cerite salts with Na_2CO_3 is not soluble in an excess of the reagent, whilst that of ThX_4 is soluble. The precipitate given by oxalic acid is soluble in a solution of ammonium oxalate. Peroxide of hydrogen (in a neutral solution at 60°) precipitates the salts of ThO_2 with great ease, as I am told by Prof. Brauner, who has devoted much labour to the investigation of thorium, and has shown that it usually contains small amounts of another metal which has not yet been separated but which undoubtedly lowers its atomic weight. This also agrees with the results of other recent but not yet completed researches, which have been incited by the radio-activity of the native compounds of thorium (see Chap. XXI., note 15a).

⁶¹ Nilson and Clève, Brauner, Moissan and Étard, Krüss, Matthews, Haber, Wyrouboff, Pissarjeffsky (who investigated the peroxides formed by the action of H_2O_2), and others obtained and investigated many compounds of thorium and showed the great interest attaching to some of its derivatives, but this is not the place to enlarge upon them.

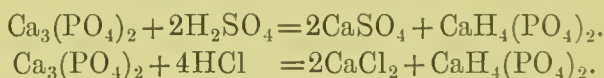
CHAPTER XIX

PHOSPHORUS AND OTHER ELEMENTS OF THE FIFTH GROUP

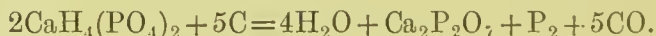
NITROGEN is the lightest as well as the typical and most widely distributed representative of the elements of the fifth group, which form a higher saline oxide of the form R_2O_5 and a hydrogen compound of the form RH_3 . Phosphorus, arsenic, bismuth, and antimony belong to the uneven series of this group. **Phosphorus** is the most widely distributed of these elements. There is hardly any mineral substance composing the mass of the earth's crust which does not contain some—though perhaps a small—amount of the salts of phosphoric acid. The soil and earthy substances in general usually contain from one to ten parts of phosphoric acid in 10,000 parts. This amount, which appears so small, has, however, a very important significance in nature. No plant can attain its natural growth if it be planted in an artificial soil completely free from phosphoric acid. Plants equally require the presence of salts of potassium, magnesium, calcium, and iron, among basic oxides, and of carbonic, sulphuric, nitric, and phosphoric anhydrides, among acid oxides. In order to increase the fertility of a more or less poor soil, the above-named nutritive elements are introduced into it by means of fertilisers. Direct experiment has proved that these substances are undoubtedly necessary to plants, but that they must be all present simultaneously and in small quantities, and that an excess, like an insufficiency, of one of these elements is necessarily followed by a bad harvest, or an imperfect growth, even if all the other conditions (light, heat, water, air) are normal. The phosphoric compounds of the soil accumulated by plants pass into the animal organism, in which these substances are assimilated in many instances in large quantities. Thus the chief component part of bones is calcium phosphate, $Ca_3P_2O_8$, and it is on this that their hardness depends.¹

¹ Dry bones consist of about one-third of gelatinous matter and about two-thirds of ash, chiefly calcium phosphate. The salts of phosphoric acid are also found in the mass of the earth as separate minerals; for example, the **apatites** contain this salt in a crystalline form, combined with calcium chloride or fluoride, $CaR_2, 3Ca_3(PO_4)_2$ (where $R = F$ or Cl), the two being sometimes in a state of isomorphous mixture. This mineral often crystallises in fine hexagonal prisms of sp. gr. 3·17 to 3·22. Vivianite is a hydrated

Phosphorus was first extracted by Brand in 1669 by the ignition of evaporated urine. After the lapse of a century, Scheele, who knew of the existence of a more abundant source of phosphorus in bones, pointed out the method which is now employed for the extraction of this element. Calcium phosphate in bones permeates a nitrogenous organic substance, which is called ossein, and forms a jelly. When bones are treated exclusively for the extraction of phosphorus, neglecting the gelatin, they are burnt, in which case all the ossein is burnt away. When, however, it is desired to preserve the gelatin, the bones are immersed in cold dilute hydrochloric acid, which dissolves the calcium phosphate and leaves the gelatin untouched; calcium chloride and acid calcium phosphate, $\text{CaH}_4(\text{PO}_4)_2$, are then obtained in the solution. When the bones are burnt directly in an open fire, their mineral components only are left as an ash, containing about 90 per cent. of calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$, mixed with a small amount of calcium carbonate and other salts. This mass is treated with sulphuric acid, and then the soluble acid calcium phosphate passes also into solution.



On evaporating the solution, the acid calcium phosphate crystallises out. The extraction of the phosphorus from $\text{CaH}_4(\text{PO}_4)_2$ consists in heating it with charcoal to a white heat. When heated, the acid phosphate, $\text{CaH}_4(\text{PO}_4)_2$, first parts with water, and forms the metaphosphate, $\text{Ca}(\text{PO}_3)_2$, which for the sake of simplicity may be regarded, like the acid salt, as composed of pyrophosphate and phosphoric anhydride, $2\text{Ca}(\text{PO}_3)_2 = \text{Ca}_2\text{P}_2\text{O}_7 + \text{P}_2\text{O}_5$. The latter, with charcoal, gives phosphorus and carbonic oxide, $\text{P}_2\text{O}_5 + 5\text{C} = \text{P}_2 + 5\text{CO}$. So that in reality a somewhat complicated reaction here takes place according to the following equation :



After the steam has come over, phosphorus and carbonic oxide distil ferrous phosphate, $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$. Phosphates of copper are frequently found in copper mines; for example, *tagilite*, $\text{Cu}_3(\text{PO}_4)_2 \cdot \text{Cu}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$. Lead and aluminium form similar salts. They are nearly all insoluble in water. The turquoise, for instance, is hydrated phosphate of alumina, $(\text{Al}_2\text{O}_3)_2 \cdot \text{P}_2\text{O}_5 \cdot 5\text{H}_2\text{O}$, coloured with a salt of copper. Sea and other waters always contain a small amount of phosphates, and, indeed, the ash of sea plants, as well as that of land plants, always contains phosphates. Deposits of calcium phosphate are often met with; they are termed **phosphorites** and **osteolites**, and are composed of the fossil remains of the bones of animals; they are used for manure. Of the same nature are the so-called guano deposits from Baker's Island, and entire strata met with in Spain, France, and the United States, and in the governments of Orloff and Kursk in Russia. It is evident that if a soil destined for cultivation contain very little phosphoric acid, the fertilisation by means of these minerals will be beneficial, but, naturally, only if the other elements necessary to plants be present in the soil.

over from the retort and calcium pyrophosphate remains behind.^{1a} As this reaction requires a white heat the retorts are soon worn out, so that the preparation of phosphorus is now carried on in furnaces in which the temperature is raised to the necessary degree by passing an electric current between carbon electrodes the charge of phosphorites or burnt bones, carbon, and sand being melted in the voltaic arc: $\text{Ca}_3\text{P}_2\text{O}_8 + 5\text{C} + 3\text{SiO}_2 = 3\text{CaSiO}_3 + 5\text{CO} + 2\text{P}$. The silicate fuses and the phosphorus distils over completely.^{1b}

As phosphorus melts at about 40° , it condenses in the receiver in a molten liquid mass, which is cast under water in moulds, and is sold in the form of sticks or discs. This is common or **yellow phosphorus**. It is a transparent, yellowish or colourless waxy substance, which is not brittle, is almost insoluble in water, and easily undergoes change in its external appearance and properties under the action of light, heat, and of various substances. It crystallises (by sublimation or from its solution in carbon bisulphide) in the regular system, and ² (in

^{1a} By subjecting the pyrophosphate to the action of sulphuric or hydrochloric acid, it is possible to obtain a fresh quantity of the acid salt from the residue, and in this manner to extract all the phosphorus. It is usual to take burnt bones; mineral phosphorites and apatites may also be employed as materials for the extraction of phosphorus for the manufacture of matches. A great many methods have been proposed for facilitating the extraction of phosphorus, but none of them differ essentially from the usual one, because the problem is dependent on the liberation of phosphoric acid by the action of acids, and on its ultimate reduction by charcoal. Thus the calcium phosphate may be mixed directly with charcoal and sand, and phosphorus will be liberated on heating the mixture, because the silica displaces the phosphoric anhydride, which gives carbonic oxide and phosphorus with the charcoal. It has also been proposed to pass hydrochloric acid over an incandescent mixture of calcium phosphate and charcoal; the acid then acts just as the silica does, liberating phosphoric anhydride, which is reduced by the charcoal. It is necessary to prevent the access of air in the condensation of the vapours of phosphorus, because they take fire very easily; hence they are condensed under water by causing the gaseous products to pass through a vessel full of water. For this purpose the condenser shown in fig. 94 is usually employed.

^{1b} It has also been proposed to combine the extraction of phosphorus in the electric furnace with the manufacture of calcium carbide, CaC_2 , by the addition of lime to the charge.

² Vernon (1891) states that ordinary (yellow) phosphorus is dimorphous. If it is melted and by careful cooling brought in a liquid form to as low a temperature as possible, it gives a variety which melts at 45.3° (the ordinary variety fuses at 44.3°), has the sp. gr. 1.827 (that of the ordinary variety is 1.818) at 13° , and crystallises in rhombic prisms (instead of in forms belonging to the cubic system). This is similar to the relation between octahedral and prismatic sulphur (Chap. XX.).

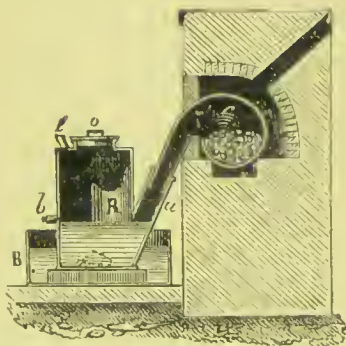


FIG. 94.—Preparation of phosphorus. The mixture is calcined in the retort *c*. The vapours of phosphorus pass through *a* into water without coming into contact with air. The phosphorus condenses in the water, and the gases accompanying it escape through *d*.

contradistinction to the other varieties) is easily soluble in carbon bisulphide, and also to some extent in other oily liquids. In this it recalls common sulphur. Its specific gravity is 1.84. It fuses at 44° (the melting-point rises rapidly with the pressure, and, according to Tammann, is about 100° at a pressure of 2,100 atmospheres), and passes into vapour at 290° (at 220° under a pressure of $\frac{1}{2}$ atmosphere; at 360° the vapour pressure is 3.2 atmospheres; and at 440° , 7.5 atmospheres); it is easily inflammable, and must therefore be handled with great caution; careless rubbing is enough to cause phosphorus to ignite. Its application in the manufacture of matches is based on this.^{2a} It emits light in the air owing to its slow ³ oxidation, and is therefore kept under water (such water is phosphorescent in the dark, like phosphorus itself). It is also very easily oxidised by various oxidising agents and takes up the oxygen from many substances.^{3a} Phosphorus enters into direct combination with many metals and with sulphur,

^{2a} According to Herr Irinyi (a Hungarian student), the first phosphorus matches were made in Austria at Roemer's works in 1837.

³ The absorption of the oxygen of the atmosphere at the ordinary temperature by a large surface of phosphorus proceeds so uniformly, regularly, and rapidly that it may serve, as Ikeda (Tokio, 1893) has shown, for demonstrating the law of the velocity (rate) of reaction, which is considered in theoretical chemistry, and states that the rate of reaction is proportional to the active mass of a substance—i.e., $dx/dt = k(A - x)$, where t is the time, A the initial mass of the reacting substance (in this case oxygen), x the amount of it which has entered into reaction, and k the coefficient of proportionality. Ikeda took a test-tube (diameter about 10 mm.) and covered its outer surface with a coating of phosphorus (by melting it in a test-tube of large diameter, inserting the smaller test-tube, and, when the phosphorus had solidified, breaking away the outer test-tube), and introduced it into a definite volume of air, contained in a Woulfe's bottle (immersed in a water-bath to maintain a constant temperature), one of whose orifices was connected with a mercury manometer showing the fall of pressure, x . Knowing that the initial partial pressure of the oxygen (in air about 750×0.209) was about 155 mm. = A , the coefficient of the rate of reaction, k , is given from the law of the variation of the rate of reaction with the mass of the reacting substance, by the equation: $k = \frac{1}{t} \log \frac{A}{A-x}$, where t is the time, counting from the commencement of the experiment, in minutes. When the surface of the phosphorus was about 11 sq. cm., the following results were actually obtained:

$t = 10$	20	30	40	50	60 minutes
$x = 10.5$	21.5	31.1	40.7	49.1	57.3 mm.
10,000 $k = 32$	32	32	33	33	33

The constancy of k is well shown in this case. The determination takes a comparatively short time, so that it may serve as a lecture experiment, and demonstrates one of the most important laws of chemical mechanics.

^{3a} Not only do oxidising agents like nitric, chromic, and similar acids act upon phosphorus, but even the alkalis are attacked—that is, phosphorus acts as a reducing agent. In fact it reduces many oxides; thus, for instance, it liberates copper from its salts. When phosphorus is heated with sodium carbonate, the latter is partially reduced to carbon. If phosphorus be placed under water slightly warmed, and a stream of oxygen be passed over it, it will burn under the water.

chlorine, &c., with development of a considerable amount of heat. It is very poisonous, although scarcely soluble in water.

Besides this, there is a red variety of phosphorus, which differs considerably from the above. **Red phosphorus** (sometimes wrongly called amorphous phosphorus) is partially formed when ordinary phosphorus remains exposed to the action of light for a long time. It is also formed in many reactions; for example, when ordinary phosphorus combines with chlorine, bromine, or oxygen, a portion of it is converted into red phosphorus. A small quantity of iodine (or selenium) is able to convert (by mere contact, as the transformation of white into red phosphorus is accompanied by the evolution of heat) a large amount of ordinary phosphorus (fused or dissolved in CS_2) into the red variety. Schrötter in Vienna (1845) investigated this variety of phosphorus, and pointed out by what methods it may be produced in considerable quantities below 250° . The conversion of ordinary into red phosphorus proceeds still more rapidly at about 500° (and therefore under a somewhat increased vapour pressure in a closed vessel). Red phosphorus is a powdery reddish-brown opaque substance of specific gravity 2.14. It does not combine so energetically with oxygen and other substances as yellow phosphorus, and evolves less heat in combining with them.¹

¹ The thermochemical determinations for phosphorus and its compounds date from the last century, when Lavoisier and Laplace burnt phosphorus in oxygen in an ice calorimeter. Andrews, Despretz, Favre, and others have also studied the subject. The most accurate and complete data are due to Thomsen. To determine the heat of combustion of yellow phosphorus, Thomsen oxidised it in a calorimeter with iodic acid in the presence of water, and a mixture of phosphorous and phosphoric acids was thus formed, the iodic acid being converted into hydriodic acid. It was first necessary to introduce two corrections into the calorimetric result obtained, one for the oxidation of the phosphorous into phosphoric acid, knowing their relative amounts by analysis, and the other for the deoxidation of the iodic acid. The result then obtained expresses the conversion of phosphorus into hydrated phosphoric acid. This must be corrected for the heat of solution of the hydrate in water, and for the heat of combination of the anhydride with water, before we can obtain the heat evolved in the reaction of P_2 with O_5 in the formation of P_2O_5 . It is natural that with so complex a method there is a possibility of many small errors, and the resultant figures will only present a certain degree of accuracy after repeated corrections by various methods. Of such a kind are the following figures determined by Thomsen, which we express in thousands of calories:— $\text{P}_2 + \text{O}_5 = 370$; $\text{P}_2 + \text{O}_5 + 3\text{H}_2\text{O} = 400$; $\text{P}_2 + \text{O}_5 + \text{a mass of water} = 405$. Hence we see that $\text{P}_2\text{O}_5 + 3\text{H}_2\text{O} = 30$; $2\text{PH}_3\text{O}_4 + \text{an excess of water} = 5$. Experiment further showed that crystallised PH_3O_4 , in dissolving in water, evolves 2.7 thousand calories, and that fused (39°) PH_3O_4 evolves 5.2 thousand calories, whence the heat of fusion of $\text{H}_3\text{PO}_4 = 2.5$ thousand calories. For phosphorous acid, H_3PO_3 , Thomsen obtained $\text{P}_2 + \text{O}_5 + 3\text{H}_2\text{O} = 250$, and the solution of crystallised H_3PO_3 in water = -0.13 , and that of fused $\text{H}_3\text{PO}_3 = +2.9$. For hypophosphorous acid, H_3PO_2 , the heats of solution are nearly the same (-0.17 and $+2.1$), and the heat of formation, $\text{P}_2 + \text{O} + 3\text{H}_2\text{O} = 75$; hence its conversion into $2\text{H}_3\text{PO}_3$ evolves 175 thousand calories, and the conversion of $2\text{H}_3\text{PO}_3$ into $2\text{H}_3\text{PO}_4$, 150 thousand calories. For the sake of comparison we will take the combination of chlorine with phosphorus, also according to Thomsen, per 2 atoms of phosphorus: $\text{P}_2 + 3\text{Cl}_2 = 151$,

Common phosphorus easily oxidises in the air; red phosphorus does not oxidise at all at the ordinary temperature; hence it does not phosphoresce in the air, and may be very conveniently kept in the form of powder. It does not, like yellow phosphorus, fuse at 44° , but at 360° . After being converted into vapour at 290° or 300° , it again passes into the ordinary variety when slowly cooled. The vapour pressure is much below that of ordinary phosphorus, being about 0.1 atmosphere at 360° , whilst that of yellow phosphorus is 3.2 atmospheres and at 500° the vapour pressures are 9 and about 20 atmospheres respectively.^{4a} Red phosphorus is not soluble in carbon bisulphide and other oily liquids, which permits of its being freed from any admixture of the ordinary phosphorus. It is not poisonous, and is used in many cases for which the ordinary phosphorus is unsuitable or dangerous; for example, in the manufacture of matches, which are then not poisonous or inflammable by accidental friction, so that here the red variety has now replaced the ordinary phosphorus.^{4b}

The heads of the 'safety' matches do not contain any phosphorus, but only substances capable of burning and of supporting combustion. Red phosphorus is spread over a surface on the box, and it is the friction against this phosphorus which ignites the matches. There is no danger of the matches taking fire accidentally, nor are they poisonous.⁵ This $P_2 + 5Cl_2 = 210$ thousand calories. In their reaction on an excess of water (with the formation of a solution), $2PCl_3 = 130$, $2PCl_5 = 247$, and $2POCl_3 = 142$ thousand calories.

Besides which we shall cite the following data given by various observers: heat of fusion for P (that is, for 31 parts of phosphorus by weight) -0.15 thousand calories: the conversion of yellow into red phosphorus for P, from $+19$ to $+27$ thousand calories: $P + H_3 = 4.3$, $HI + PH_3 = 24$, $PH_3 + HBr = 22$ thousand calories.

^{4a} Bakhuis Roozeboom, Tammann, and others have expressed graphically the complex relations between the volume, temperature, and pressure for phosphorus. The student will find details of this subject in works on physical chemistry (the doctrine of phases).

^{4b} Ordinary phosphorus takes fire at a temperature (60°) at which no other known substance will burn. Its application to the manufacture of matches is based on this property. In order to illustrate the great inflammability of common (yellow) phosphorus, its solution in carbon bisulphide may be poured over paper: this solvent quickly evaporates, and the free phosphorus spread over a large surface takes fire spontaneously, notwithstanding the cooling effect produced by the evaporation of the bisulphide. The majority of **phosphorus matches** are composed of common phosphorus mixed with some oxidising substance which easily gives up oxygen, such as lead dioxide, potassium chlorate, nitre, &c. For this purpose common phosphorus is carefully triturated under warm water containing a little gum; lead dioxide and potassium nitrate are then added to the resultant emulsion, and the match ends, previously coated with sulphur or paraffin, are dipped into this preparation. After this the matches are dipped into a solution of gum and shellac in order to preserve the phosphorus from the action of the air. When such a match containing particles of yellow phosphorus is rubbed over a rough surface, it becomes (especially at the point of rupture of the brittle gummy coating) slightly heated, and this is sufficient to cause the phosphorus to take fire and burn at the expense of the oxygen of the other ingredients.

⁵ In the so-called 'safety' or Swedish matches a mixture of red phosphorus and glass

red phosphorus is prepared by heating ordinary phosphorus at 230° to 270° ; it is evident that this must be done in an atmosphere incapable of supporting combustion—for example, in nitrogen, carbonic anhydride, steam, &c. On a large scale, ordinary phosphorus is placed in closed iron vessels,^{5a} and immersed in a bath of different proportions of tin and lead, by which means the temperature of 250° , necessary for the conversion, is easily attained. It is kept at this temperature for some time. The temperature is at first cautiously raised, and the air is thus partially expelled by the heat, and also by the evolution of steam (the phosphorus is damp when put in), while the remaining oxygen is also partially absorbed by the phosphorus, so that an atmosphere of nitrogen is produced in the iron vessel. Red phosphorus enters into all the reactions proper to yellow phosphorus, only with greater difficulty and more slowly; ⁶ and, as its vapour pressure (volatility) is less than that

forms the surface on which the matches are struck, and the matches themselves do not contain any phosphorus at all, but a mixture of antimonious sulphide, Sb_2S_3 (or similar combustible substances) and potassium chlorate (or other oxidising agents). The combustion, when once started by contact with the red phosphorus, proceeds by itself at the expense of the inflammatory and combustible elements contained in the tip of the match. The mixture forming the heads of the 'safety' matches has the following approximate composition: 55–60 parts of chlorate of potassium, 5–10 parts of peroxide of manganese (or of $\text{K}_2\text{Cr}_2\text{O}_7$), about 1 part of sulphur or charcoal, about 1 part of pentasulphide of antimony, Sb_2S_5 , and 30–40 parts of rouge and powdered glass. This mixture is stirred up in gum or glue, and the matches are dipped into it. The paper on which the matches are struck is coated with a mixture of red phosphorus and trisulphide of antimony, Sb_2S_3 , stirred up in dextrine.

^{5a} Phosphorus only acts on iron at a red heat. The boiler is provided with a safety valve and gas-conducting tube, which is immersed in mercury or other liquid to prevent the admission of air into the boiler.

⁶ The specific heat of the yellow variety is 0.189, and is greater than that of the red variety, which is 0.170. The sp. gr. of the yellow form is 1.84, and that of the red prepared at 260° , 2.15, and of that prepared at 580° and above (i.e., 'metallic' phosphorus; see below), 2.34. At 230° the pressure of the vapour of ordinary phosphorus is 514 millimetres of mercury, and of the red, 0—that is to say, red phosphorus does not form any vapour at this temperature; at 447° the vapour pressure of ordinary phosphorus is at first 5,500 mm., but it gradually diminishes with the formation of red phosphorus, for which it is equal to 1,636 mm.

Hittorf, by heating the lower portion of a closed tube containing red phosphorus to 530° and the upper portion to 447° , obtained crystals of the so-called 'metallic' phosphorus at the upper extremity. As the vapour pressures (according to Hittorf, at 530° the vapour of yellow phosphorus is 8,040 mm., that of red, 6,139 mm., and that of metallic, 4,130 mm.) and reactions are different, **metallic phosphorus** may be regarded as a distinct variety. It is still less energetic in its chemical reactions than red phosphorus, and it is denser than the two preceding varieties, its sp. gr. being 2.34. It does not oxidise in the air, is crystalline, and has a metallic lustre. It is obtained when ordinary phosphorus is heated with lead for several hours at 400° in a closed vessel from which the air has been exhausted. The resultant mass is then treated with dilute nitric acid, which first dissolves the lead (phosphorus is electro-negative to lead, and does not therefore, act on the nitric acid at first) and leaves brilliant rhombohedral crystals of phosphorus of a dark-violet colour with a slight metallic lustre, which conduct an electric current incomparably better than the yellow variety; this also is characteristic

of the yellow variety, it may be supposed that polymerisation takes place in the passage of the yellow into the red modification, just as in the passage of cyanogen into paracyanogen, or of cyanic acid into cyanuric acid (Chap. IX., notes 39a and 48).

The vapour of phosphorus is colourless ; its density remains almost constant between 300° and $1,000^{\circ}$ (Dumas, 1833 ; Mitscherlich, Deville and Troost, 1859, and others ; it falls slightly as the temperature rises). Referred to hydrogen, it is 62, and therefore corresponds with a molecular weight of 124, i.e., the molecule of phosphorus in a state of vapour contains P_4 . The reader will remember that the molecule

of the metallic state of phosphorus. However, metallic phosphorus may be a well-crystallised variety of the red modification.

The researches of Lemoine partially explain the passage of yellow (ordinary) phosphorus into the other varieties. He heated a closed glass globe, containing either ordinary or red phosphorus, in the vapour of sulphur (440°), and then determined the amount of the red and yellow varieties after various periods of time, by treating the mixture with carbon bisulphide. It appeared that after the lapse of a certain time a mixture of definite composition is obtained from both—that is, between the red and yellow varieties a state of equilibrium sets in like that of dissociation, or that observed in double decompositions. But at the same time, the progress of the transformation appeared to be dependent on the quantity of phosphorus taken relatively to the volume of the globe (i.e., upon the pressure). Neglecting the latter, we will cite as an example the amounts of the red phosphorus transformed into the ordinary, and of the ordinary not converted into red, per 30 grams of red or yellow taken per litre capacity of the globe, heated to 440° . When red phosphorus was taken, 4.75 grams of yellow phosphorus were formed after two hours, four grams after eight hours, three grams after twenty-four hours, and the last limit remained constant on further heating. When thirty grams of yellow phosphorus were taken, five grams remained unaltered after two hours, four grams after eight hours, and after twenty-four hours and more, three grams as before. Troost and Hautefeuille showed that liquid phosphorus in general changes more easily into the red than does phosphorus vapour, which, however, is able, although slowly, to deposit red phosphorus according to the relation between t and V .

The question presents itself as to whether phosphorus in a state of vapour is the ordinary or some other variety. Hittorf (1865) collected many data for the solution of this problem, which leave no doubt that (as experimental figures show) the density of the vapour of phosphorus is always the same, although the vapour pressure of the different varieties and their mixtures is very variable. This shows that the different varieties of phosphorus only occur in a liquid and a solid state. Strictly speaking, the vapour of phosphorus is a particular state of this substance, and the molecular formula P_4 refers only to it, and not to any other definite state of phosphorus. But the method of the depression of the freezing-point (Chap. VII.) showed that in a benzene solution, the fall of the freezing-point indicates for ordinary phosphorus a molecule P_4 , judging by the determinations of Paterno and Nasini (1888), Hirtz (1890), and Beckmann (1891), who obtained for sulphur by the same method a molecular weight corresponding with S_8 , in conformity with the vapour density. Further research in this direction will perhaps show the possibility of finding the molecular weight of red phosphorus, if a means be discovered for dissolving it without converting it into the yellow variety.

I think it will not be out of place here to draw the reader's attention to the fact that red phosphorus stands nearer to nitrogen, whose molecule is N_2 , in its small inclination towards chemical reactions, although, judging by its small vapour pressure, it must be more complex than ordinary (yellow and white) phosphorus. The conception of polymerisation alone cannot therefore account for everything in this instance.

of nitrogen contains N_2 , that of sulphur S_6 or S_2 , and that of oxygen O_2 or O_3 .

The chemical energy of phosphorus in a free state more nearly approaches that of sulphur than nitrogen. Phosphorus is combustible and inflames at 60° ; but having in the act of combination parted with a portion of its energy in the form of heat it becomes analogous to nitrogen, so long as there is no question of its reduction back again into phosphorus. Nitric acid is easily reduced to nitrogen, whilst phosphoric acid is reduced with very much greater difficulty. All the compounds of phosphorus are less volatile than those of nitrogen. Nitric acid, HNO_3 , is easily distilled; metaphosphoric acid, HPO_3 , is generally said to be non-volatile; triethylamine, $N(C_2H_5)_3$, boils at 90° , and triethyl-phosphine, $P(C_2H_5)_3$, at 127° .

Phosphorus not only combines easily and directly with oxygen, but also with chlorine, bromine, iodine, sulphur, and with certain metals, and red phosphorus when heated combines with hydrogen also.^{6a} Thus, for instance, when fused with sodium under naphtha, phosphorus gives the compound Na_3P_2 . Zinc, absorbing the vapour of phosphorus, gives the phosphide Zn_3P_2 (sp. gr. 4.76); tin, SnP ; copper, Cu_2P ; and even platinum combines with phosphorus (PtP_2 , sp. gr. 8.77).^{6b} Iron, when combined with even a small quantity of phosphorus, becomes brittle.⁷ Some of these compounds of phosphorus are obtained by the action of phosphorus on the solutions of metallic salts, and by the ignition of metallic oxides in the vapour of phosphorus, or by heating mixtures of

^{6a} Retgers (see further on) showed this in 1894, and observed that As when heated, also combines with hydrogen. The flame of hydrogen gas is coloured green by the presence of the smallest trace of free phosphorus (carried in the vapour of water).

^{6b} The capacity of mercury (Chap. XVI., note 25a) to give unstable compounds with nitrogen gives rise to the supposition that similar compounds exist with phosphorus also. Such a compound was obtained by Granger (1892) by heating mercury with iodide of phosphorus in a closed tube at 275° – 300° . After removing the iodide of mercury formed, there remain fine rhombic crystals having a metallic lustre, and the composition Hg_3P_2 . This compound is stable, does not alter at the ordinary temperature, and only decomposes at a red heat; when heated in air it burns with a flame. Nitric or hydrochloric acid does not act upon it, but it is easily decomposed by aqua regia.

⁷ The metallic compounds of phosphorus possess a great chemical interest, because they show a transition from metallic alloys to the sulphides, halogen salts, and oxides, and on the other hand to the nitrides. Although there are already many fragmentary data on the subject, the interesting province of the metallic phosphides cannot yet be regarded as in any way generalised. The varied applications (phosphor-iron, phosphor-bronze, &c.), which the phosphides have recently acquired should give a strong incentive to the complete and detailed study of this subject, which would, in my opinion, help to the explanation of chemical relations, beginning with alloys (solutions) and ending with salts and the compounds of hydrogen (hydrides), because the phosphor-metals, as is proved by direct experiment, stand in the same relation to phosphoretted hydrogen as the sulphides do towards sulphuretted hydrogen, or as the metallic chlorides to hydrochloric acid.

phosphates with charcoal and metals. Phosphides do not exhibit the external properties of salts, which are so clearly seen in the chlorides and still distinctly observable in the sulphides. **The phosphides of the metals** of the alkalis and of the alkaline earths are even immediately and very easily decomposed by water, whereas this is found to be the case with only a very few sulphides, and still more rarely and indistinctly with the chlorides. We may take calcium phosphide as an example.^{7a} Phosphorus is laid in a deep crucible, and covered with a clay plug, over which lime is strewn. At a red heat the vapours of phosphorus combine with the oxygen of the lime and form phosphoric anhydride, which forms a salt with another portion of the lime, while the liberated calcium combines with the phosphorus and forms calcium phosphide. Its composition is not quite certain; it may be CaP (corresponding with liquid phosphoretted hydrogen). This substance is remarkable for the following reaction: if it is thrown into water—or, better still, a dilute solution of hydrochloric acid—bubbles of gas are evolved, which take fire spontaneously in the air and form white rings. This is owing to the fact that the liquid hydrogen phosphide, PH_2 , is first formed, thus, $\text{CaP} + 2\text{HCl} = \text{CaCl}_2 + \text{PH}_2$, and this, owing to its instability, very easily splits up into the solid phosphide, P_2H , and the gaseous one PH_3 : $5\text{PH}_2 = \text{P}_2\text{H} + 3\text{PH}_3$; ^{7b} the latter corresponds with ammonia. The mixture of the gaseous and liquid phosphides takes fire spontaneously in the air, forming phosphoric acid. The same hydrogen phosphides are formed when water acts on sodium phosphide (Na_3P_2). A similar mixture of gaseous, liquid and solid phosphoretted hydrogen (Retgers, 1894) is formed by heating (in a glass tube) red phosphorus in a stream of dry hydrogen. Hence we see that there are **three compounds of phosphorus with hydrogen**: (1) The solid yellow phosphide, P_2H (more probably P_4H_2), is obtained by the action of strong hydrochloric acid on sodium phosphide; it takes fire when struck or when heated to 175° . (2) The liquid, PH_2 , or more correctly expressed as the molecule, P_2H_4 , is a colourless liquid which takes fire spontaneously in the air, boils at 60° , is very unstable, and is easily decomposed (by light or hydrochloric acid) into the two other phosphides of hydrogen. It is prepared by passing the gases evolved by the action of water

^{7a} Many other compounds of phosphorus are also capable of forming phosphoretted hydrogen. Thus BP also gives PH_3 (see Chap. XVII., note 12). The following is another easy method for preparing PH_3 . A mixture of 1 part of zinc dust (fine) and 2 parts of red phosphorus is heated in an atmosphere of hydrogen (the mixture burns in air). Combination takes place, accompanied by a flash, and a grey mass of Zn_3P_2 is formed which gives PH_3 when treated with dilute H_2SO_4 .

^{7b} Moissan obtained a phosphide of calcium having the composition Ca_3P_2 by heating $\text{Ca}_3(\text{PO}_4)_2$ in the electric furnace with carbon. With water it gives PH_3 without forming PH_2 .

on calcium phosphide through a freezing mixture.⁸ And, lastly, (3), gaseous hydrogen phosphide, *phosphine*, PH_3 , which is distinguished as being the most stable. It is a colourless gas, which does not take fire in the air. It has an odour of garlic, and is very poisonous. It resembles ammonia in certain of its properties.^{8a} It is easily decomposed by heat, like ammonia, forming phosphorus and hydrogen; but it is very slightly soluble in water, and does not saturate acids, although with some of them it forms compounds which resemble ammonium salts in their form and properties. Among them **phosphonium iodide**, PH_4I , analogous to ammonium iodide, is worthy of notice. This compound crystallises on sublimation in well-formed lustrous cubes. It does not, however, enter into those reactions of double decomposition which are proper to sal-ammoniac, because its saline properties are very feebly developed; even water decomposes it. Phosphoretted hydrogen also combines, like ammonia, with certain chloranhydrides; but they are decomposed by water, with the evolution of phosphine. Ogier (1880) showed that hydrochloric acid also combines with phosphine under a pressure of 20 atmospheres at $+18^\circ$, and under the ordinary pressure at -35° , forming the crystalline phosphonium chloride, PH_4Cl , corresponding with sal-ammoniac. Hydrobromic acid does the same with greater ease, and hydriodic acid with still greater facility, forming phosphonium iodide, PH_4I ,⁹ which acts in many cases as a powerful reducing agent.

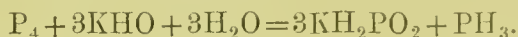
⁷ Discovered by Thénard, the spontaneous inflammability of the hydride PH_2 in air is very remarkable, and it is particularly interesting that its analogues in composition, $\text{P}(\text{C}_2\text{H}_5)_2$ (the formula must be doubled) and $\text{Zn}(\text{C}_2\text{H}_5)_2$, also take fire spontaneously in air.

^{8a} The analogy between PH_3 and NH_3 is particularly clear in the hydrocarbon derivatives. Just as NH_2R , NHR_2 , and NR_3 , where R is CH_3 and other hydrocarbon radicles, correspond with NH_3 , so there exist similar compounds corresponding with PH_3 . These compounds form a branch of organic chemistry. The action of PH_3 on a solution of Na or K in liquid NH_3 leads to the formation of PNaH_2 or PKH_2 , resembling the amides of Na and K.

⁹ The periodic law and direct experiment (the molecular weight) show that PH_3 is the normal compound of P and H, and that it is more simple than PH_2 or P_2H_4 , just as methane, CH_4 , is more simple than ethane, C_2H_6 , whose empirical composition is CH_3 . The formation of liquid phosphoretted hydrogen may be understood from the law of substitution. The univalent radicle of PH_3 is PH_2 , and if it is combined with H in PH_3 it replaces H in liquid phosphoretted hydrogen, which thus gives P_2H_4 . This substance corresponds with free amidogen (hydrazine), N_2H_4 (Chap. VI.)⁴ Probably P_2H_4 is able to combine with HI, and perhaps also with 2HI , or other molecules—that is, to give a substance corresponding to phosphonium iodide.

Phosphonium iodide, PH_4I , may be prepared, according to Baeyer, in large quantities in the following manner:—100 parts of phosphorus are dissolved in dry carbon bisulphide in a tubulated retort; when the mixture has cooled, 175 parts of iodine are added little by little, and the carbon bisulphide is then distilled off, this being done towards the end of the operation in a current of dry carbonic anhydride at a moderate temperature. The neck of the retort is then connected with a wide glass tube, and the

Phosphoretted hydrogen or phosphine, PH_3 , is generally prepared by the action of caustic potash on phosphorus.¹⁰ Small pieces of phosphorus are dropped into a flask containing a strong solution of caustic potash and heated. Potassium hypophosphite, H_2KPO_2 , is then obtained in solution; gaseous phosphoretted hydrogen is evolved:



Liquid phosphoretted hydrogen (and free hydrogen) is also formed, together with the phosphine, so that the gaseous product, on escaping from the water into the air, takes fire spontaneously, forming beautiful white rings of phosphoric acid. In this experiment, as in that with calcium phosphide, it is the liquid, P_2H_4 , that takes fire; but the phosphine ignited by it also burns, $\text{PH}_3 + \text{O}_4 = \text{PH}_3\text{O}_4$. The same phosphoretted hydrogen, PH_3 , may be obtained pure, and not spontaneously combustible, by igniting the hydrates of phosphorous acid ($4\text{PH}_3\text{O}_3 = \text{PH}_3 + 3\text{PH}_3\text{O}_4$) and hypophosphorous acid ($2\text{PH}_3\text{O}_2 = \text{PH}_3 + \text{PH}_3\text{O}_4$); or, more simply, by the decomposition of calcium phosphide by hydrochloric acid, because then all the liquid phosphide,

tubulure fitted with a funnel furnished with a stopcock and containing 50 parts of water. This water is added drop by drop to the phosphorous iodide, and a violent reaction takes place, with the evolution of hydriodic acid and phosphonium iodide. The latter collects as crystals in the glass tube and in the retort itself. It is purified by further distillations; more than 100 parts may be obtained. Baeyer expresses the reaction by the equation, $\text{P}_2\text{I} + 2\text{H}_2\text{O} = \text{PH}_4\text{I} + \text{PO}_2$; and the compound PO_2 may be represented as phosphorous phosphoric anhydride: $\text{P}_2\text{O}_3 + \text{P}_2\text{O}_3 = 4\text{PO}_2$. As a better proportion we may take 400 grams of phosphorus, 680 grams of iodine, and 240 grams of water, and express the formation thus: $13\text{P} + 9\text{I} + 21\text{H}_2\text{O} = 3\text{H}_4\text{P}_2\text{O}_7 + 7\text{PH}_4\text{I} + 2\text{HI}$ (Chap. XI., note 77).

Phosphonium iodide and even phosphine act as reducing agents in solutions of many metallic salts. Cavazzi showed that with a solution of sulphurous anhydride phosphine gives sulphur and phosphoric acid. At a red heat steam acts upon phosphorus according to the equation, $2\text{P} + 3\text{H}_2\text{O} = \text{PH}_3\text{O}_2 + \text{PH}_3$.

¹⁰ The air must first be expelled from the flask by hydrogen, or some other gas which will not support combustion, as otherwise an explosion might take place owing to the spontaneous inflammability of the phosphoretted hydrogen.

The combustion of phosphoretted hydrogen in oxygen also takes place under water when the bubbles of both gases meet, and is very brilliant. The phosphoretted hydrogen obtained by the action of phosphorus on caustic potash always contains free hydrogen, and often even the greater part of the gas evolved consists of hydrogen. *Pure phosphoretted hydrogen* (not containing hydrogen or liquid or solid phosphides) is obtained by the action of a solution of potash on phosphonium iodide: $\text{PH}_4\text{I} + \text{KHO} = \text{PH}_3 + \text{KI} + \text{H}_2\text{O}$ (in just the same way as ammonia is liberated from ammonium chloride). The reaction proceeds easily, and the purity of the gas is seen from the fact that it is entirely absorbed by bleaching powder and is not spontaneously inflammable. Its mixture with oxygen explodes when the pressure is diminished (Chap. XVIII., note 5). The vapours of bromine, nitric acid, &c., cause it to again acquire the property of inflaming in the air; that is, they partially decompose it, forming the liquid hydride, P_2H_4 . Oppenheim showed that when red phosphorus is heated at 200° with hydrochloric acid in a closed tube it forms the compound $\text{PCl}_3(\text{H}_3\text{PO}_3)$, together with phosphine.

P_2H_4 , is decomposed into non-volatile P_2H and gaseous PH_3 . Pure phosphine liquefies when cooled to -90° , boils at -85° , and solidifies at -135° (Olszewski). When phosphorus burns *in an excess*^{10a} of dry oxygen, then only **phosphoric anhydride**, P_2O_5 , is formed. It is prepared by dropping pieces of phosphorus through a wide tube, fixed into the upper neck of a large glass globe, on to a cup suspended in the centre of the globe. These lumps are set alight by touching them with a hot wire, and the phosphorus burns into P_2O_5 . The dry air necessary for its combustion is forced into the globe through a lateral neck, and the white flakes of phosphoric anhydride formed are carried by the current of air through a second lateral neck into a series of Woulfe's bottles, where they settle as friable white flakes. Phosphoric anhydride may also be formed by passing dry air through a solution of phosphorus in carbon bisulphide. All the materials for the preparation of this substance must be carefully dried, because it **combines** with great eagerness **with water**, at the same time developing a large amount of heat and forming metaphosphoric acid, HPO_3 , from which the water cannot be separated by heat. Phosphoric anhydride is a colourless snowlike substance, which attracts moisture from the air with the utmost avidity.

It fuses at a red heat, and then **volatilises** (it is therefore purified by distillation).^{10b} Its affinity for water is so great that it takes it up from many substances. Thus, it converts sulphuric acid into sulphuric

^{10a} If there is a deficiency of oxygen, **phosphorous anhydride**, P_2O_3 , is formed. It was obtained by Thorpe and Tutton (1890) and is easily volatilised, melts at 22.5° , boils without change (in an atmosphere of N_2 or CO_2) at 173° , and is therefore easily separated from P_2O_5 , which volatilises with difficulty. The vapour density shows that the molecular weight is double, i.e., P_4O_6 (like As_2O_3). Although colourless, phosphorous anhydride (its density in a state of fusion at 24° is 1.936) turns yellow and reddens in sunlight (possibly red phosphorus separates out?), and decomposes at 400° forming hypophosphorous anhydride, P_2O_4 (note 11) and phosphorus. It passes into P_2O_5 in air or oxygen, and when slightly heated in oxygen becomes luminous, and ultimately takes fire. Cold water slowly transforms P_2O_3 into phosphoric acid, but hot water gives an explosion and leads to the formation of PH_3 , ($P_4O_6 + 6H_2O = PH_3 + 3PH_3O_4$). Alkalies act in the same manner. It takes fire in chlorine and forms $POCl_3$ and PO_2Cl , and combines with sulphur at 160° , forming $P_2S_2O_3$ (the molecular formula is double this), a substance which volatilises *in vacuo* and is decomposed by water into H_2S and phosphoric acid, i.e., it may be regarded as P_2O_5 , in which O_2 has been replaced by two atoms of sulphur. Judging from the above, the mixture of P_2O_3 and P_2O_5 formed in the combustion of phosphorus in air is transformed into P_2O_5 in an excess of oxygen.

^{10b} Phosphoric anhydride, P_2O_5 , is obtained in a crystalline form when carefully distilled (in an atmosphere of CO_2), and it then boils at 250° . But with the amorphous variety (which is easily and generally formed, especially at 400°) the vapour pressure is very small at 250° (Hautefeuille), and in this form the anhydride, fused at a red heat, solidifies into a vitreous mass, which cracks after being kept some time, and which combines less vigorously with water than the crystalline form. The vitreous modification, however, also passes into the crystalline variety when distilled. This is probably another instance of polymerisation like that we shall presently meet with in metaphosphoric acid.

anhydride, while carbohydrates (wood, paper) are carbonised and give up the elements of water when brought into contact with it.

When *moist* phosphorus slowly oxidises in the air, it not only forms phosphorous and phosphoric acids, but also **hypophosphoric acid**, $\text{H}_4\text{P}_2\text{O}_6$, which when in a dry state easily splits up at 60° into phosphorous and metaphosphoric acids ($\text{H}_4\text{P}_2\text{O}_6 = \text{H}_3\text{PO}_3 + \text{HPO}_3$), but differs from a mixture of these acids in that it forms well-characterised salts, of which the sodium salt, $\text{H}_2\text{Na}_2\text{P}_2\text{O}_6$, is but slightly soluble in water (the sodium salts of phosphoric and phosphorous acids are easily soluble), and does not act as a reducing agent, like mixtures containing phosphorous acid.¹¹

Judging by the general law of the formation of acids (Chap. XV.), the series of phosphorus compounds should include the following **ortho-acids** and their corresponding anhydrides, answering to phosphoretted hydrogen, H_3P :—

H_3PO_4 , phosphoric acid, and	P_2O_5 , anhydride,
H_3PO_3 , phosphorous acid, and	P_2O_3 , anhydride,
H_3PO_2 , hypophosphorous acid, and	P_2O , anhydride. ¹²

¹¹ Salzer proved the existence of **hypophosphoric acid** (it is also called subphosphoric acid), in which many chemists did not believe. Drave (1888) and Rammelsberg (1892) investigated its salts. It may be obtained in a free state by the following method. The solution of acid produced by the slow oxidation of moist phosphorus is mixed with a solution (25 per cent.) of sodium acetate. A salt, $\text{Na}_3\text{H}_2\text{P}_2\text{O}_6 \cdot 6\text{H}_2\text{O}$, crystallises out on cooling; it is soluble in 45 parts of water, and gives a precipitate of $\text{Pb}_2\text{P}_2\text{O}_6$ with lead salts ($\text{Ag}_2\text{P}_2\text{O}_6$ with salts of silver). The lead salt is decomposed by a current of hydrogen sulphide, when lead sulphide is precipitated, while the solution, evaporated under the receiver of an air-pump, gives crystals of $\text{H}_4\text{P}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$, which readily lose water and give $\text{H}_4\text{P}_2\text{O}_6$. The salts in which the H_1 is replaced by Ni_2 , or NiNa_2 , or CdNa_2 , &c., are insoluble in water.

In order to see the relation between phosphoric acid and hypophosphoric acid, which does not contain the elements of phosphorous acid (because it does not reduce either gold or mercury from their solutions) but which nevertheless is capable of being oxidised (for example, by potassium permanganate) into phosphoric acid, it is simplest to apply the law of substitution. This clearly indicates the relation between oxalic acid, $(\text{COOH})_2$, and carbonic acid, $\text{OH}(\text{COOH})$. The relation between the above acids is exactly the same if we express phosphoric acid as $\text{OH}(\text{POO}_2\text{H}_2)$, because in this case $\text{P}_3\text{H}_4\text{O}_7$, or $(\text{POO}_2\text{H}_2)_2$, will correspond with it just as oxalic does with carbonic acid. A similar relationship exists between hyposulphuric or dithionic acid, $(\text{SO}_2\text{OH})_2$, and sulphuric acid, $\text{OH}(\text{SO}_2\text{OH})$, as we shall find in the following chapter. Dithionic acid corresponds with the anhydride S_2O_5 , intermediate between SO_2 and SO_3 ; oxalic acid with C_2O_3 , intermediate between CO and CO_2 ; hypophosphoric acid corresponds with the anhydride P_2O_4 , which is intermediate between P_2O_3 and P_2O_5 , and is the analogue of N_2O_4 .

¹² Besides the hydrates enumerated, a compound, PH_3O , should correspond with PH_3 . This hydrate, which is analogous to hydroxylamine, is not known in a free state, but it is known as triethylphosphine oxide, $\text{P}(\text{C}_2\text{H}_5)_3\text{O}$, which is obtained by the oxidation of triethylphosphine, $\text{P}(\text{C}_2\text{H}_5)_3$. It must be observed that there may also be lower oxides of phosphorus corresponding with PH_3 , like N_2O and NO , and there are even indications of the formation of such compounds, but the data concerning them cannot be considered to be firmly established. Among the lower oxygen compounds of phosphorus, the **suboxide**

All these substances are known in a free state, and the types (but not the physical properties, owing to their being polymerised; for instance P_2O_3 gives a molecule P_4O_6 , note 10a) of the anhydrides correspond to those of nitrogen, N_2O_5 (nitric anhydride), N_2O_3 (nitrous) and N_2O (hyponitrous),^{12a} while the hydrates in their normal state contain more water than the corresponding nitrogen compounds and are orthohydrates containing as much hydrogen as the higher hydrogen compound, whereas the metahydrates for nitrogen are equal to orthohydrates less one molecule of water. However, phosphoric anhydride (P_2O_5) with a small quantity of water does not at first give orthophosphoric acid, PH_3O_4 , but a compound $P_2O_5 \cdot H_2O$, or PHO_3 , whose composition corresponds with that of nitric acid: this is **metaphosphoric acid**. Even with an excess of water, combining with phosphoric anhydride, this metaphosphoric acid, and not the ortho-compound, passes at first into solution. Metaphosphoric acid in solution only passes into orthophosphoric acid when the solution is heated or after a lapse of time.

Orthophosphoric acid¹³ is obtained by oxidising phosphorus with nitric acid until the phosphorus passes entirely into solution and the lower oxides of nitrogen cease to be evolved. Red phosphorus is taken as a rule; if white phosphorus is used, the reaction takes place best with dilute nitric acid, and when aided by heat. The resultant solution is

P_4O obtained by Michaelis (1900) is of particularly frequent occurrence. It is formed in the oxidation of phosphorus, but usually together with the other oxides. It is obtained in a pure state by the action of acetic anhydride upon hypophosphorous acid by the elimination of water, phosphorous acid being also formed: $5PH_3O_2 = 6H_2O + PH_3O_3 + P_4O$. The same P_4O is formed if ordinary phosphorus is covered with a mixture of a 10 per cent. solution of $NaHO$ with twice its volume of alcohol; hydrogen is then evolved and the phosphorus forms a dark-red solution, from which acids precipitate P_4O as a yellow powder of sp. gr. 1.9, which splits up into P_2O_5 and phosphorus when heated (in a state of dryness). It is redissolved by an alcoholic solution of $NaHO$, forming a red solution which gradually becomes colourless with the formation of hydrogen and hypophosphorous acid, $P_4O + 7H_2O = 4PH_3O_2 + H_2$, which proves the connection between P_4O and P_2O (note 12a). There is a solid phosphide of hydrogen, P_1H_2 , corresponding with P_1O .

^{12a} The compound P_2O , corresponding to hypophosphorous acid and N_2O , or **phosphorus dioxide**, was obtained by Besson (1897) by heating a mixture of PH_3O_3 and PCl_3 , which leads first to the dehydration of the phosphorous acid and formation of P_2O_3 , the latter then splitting up: $2P_2O_3 = P_2O_5 + P_2O$. The same substance is obtained by heating phosphonium bromide (note 9) with $POCl_2$ (note 13). Phosphorus dioxide forms a reddish-yellow powder which decomposes at 130° . Water has no action on it.

¹³ Phosphoric acid, being a soluble and almost non-volatile substance, cannot be prepared, like hydrochloric and nitric acids, by the action of sulphuric acid on the alkali phosphates, although it is partially liberated in the process. For this purpose the phosphates of barium or lead may be taken, because they give insoluble precipitates; thus, $Ba_3(PO_4)_2 + 3H_2SO_4 = 3BaSO_4 + 2H_3PO_4$. Bone ash contains, besides calcium phosphate, sodium and magnesium phosphates, and fluorides and other salts, so that it cannot give directly a pure phosphoric acid.

evaporated to a syrup. If a weighed quantity of phosphorus be taken, a crystalline mass of the acid can be obtained by evaporating the solution until it consists only of the quantity¹¹ of phosphoric acid corresponding with the amount of phosphorus taken (from 31 parts of P, 98 parts of acid). The acid fuses at $+39^{\circ}$, the specific gravity of the liquid being 1.88. Phosphorus pentachloride, PCl_5 , and the oxychloride, POCl_3 (see further on), give orthophosphoric acid and hydrochloric acid with water. The two other varieties of phosphoric acid, with which we shall presently become acquainted, give the same ortho-acid under the influence of acids, with particular ease when boiled and more slowly in the cold. By itself, orthophosphoric acid (either in solution or when dry) does not pass into the other varieties; it does not oxidise, and therefore presents the limiting and stable form. When heated to 200° , it loses water and passes into pyrophosphoric acid, $2\text{H}_3\text{PO}_4 = \text{H}_2\text{O} + \text{H}_4\text{P}_2\text{O}_7$, whilst at an incipient red heat (about 350°) it loses twice as much water and is converted into metaphosphoric acid, $\text{H}_3\text{PO}_4 = \text{H}_2\text{O} + \text{HPO}_3$. In aqueous solution, orthophosphoric acid differs clearly from pyro- or meta-phosphoric acids, because the solutions of these latter acids give different reactions: thus, orthophosphoric acid does not precipitate albumin, does not give a precipitate with barium chloride, and forms a yellow precipitate of silver orthophosphate, Ag_3PO_4 , with silver nitrate after being saturated with alkalis; whilst a solution of pyrophosphoric acid, $\text{H}_4\text{P}_2\text{O}_7$, although it does not precipitate albumin or barium chloride, gives a white precipitate of silver pyrophosphate, $\text{Ag}_4\text{P}_2\text{O}_7$, with silver nitrate; and a solution of metaphosphoric acid, HPO_3 , precipitates both albumin and barium chloride, and gives a white precipitate of silver metaphosphate, AgPO_3 , with silver nitrate. These points of distinction were studied by Graham, and are exceedingly instructive. They show that the solution of a substance does not determine the maximum of chemical combination with water, that solutions may contain various degrees of combination with water, and that there is a great difference between the water serving for solution and that entering into chemical combination. Graham's experiments also showed that the water whose removal or combination determines the difference between ortho-, meta-, and pyro-phosphoric acids differs

¹¹ If this is not done, the orthophosphoric acid, PH_3O_4 , loses a portion of its water, and then, as with an excess of water, it does not crystallise.

Phosphorus and hence also its preparations, usually contain arsenic. It may be separated from solutions of phosphoric acid by sulphuretted hydrogen. This induced Fittica (1900) to assume that he had succeeded in partly converting phosphorus into arsenic. C. Winkler afterwards proved that this was only a repetition of the mistake which has often given rise to the notion of the elements being transmutable into each other. Such mistakes are likely often to recur in insufficiently careful researches.

distinctly from water of crystallisation, for he obtained the salts of ortho-, meta-, and pyro-phosphoric acids with water of crystallisation, and they differed in their reactions like the acids themselves. This water of crystallisation was expelled with greater ease than the water of constitution of the hydrates in question.^{14a}

Orthophosphoric acid has a pleasant acid taste and a distinctly acid reaction; it is used as a medicine, and is not poisonous (phosphorous acid is poisonous). Alkalies, like sodium, potassium, and ammonium hydroxides, saturate the acid properties of phosphoric acid when taken in the ratio $2\text{NaHO} : \text{H}_3\text{PO}_4$ —that is, when salts of the composition HNa_2PO_4 are formed. When taken in the ratio $\text{NaHO} : \text{H}_3\text{PO}_4$, a salt having an acid reaction is obtained, and with $3\text{NaHO} : \text{H}_3\text{PO}_4$ —that is, when the salt Na_3PO_4 is formed—an alkaline reaction is obtained. Hence many chemists (Berzelius) even regarded the salts of composition R_2HPO_4 as normal, and considered phosphoric acid to be dibasic.^{14b} Orthophosphoric acid is tribasic, because it contains three equivalents of hydrogen replaceable by metals, forming salts, such as NaH_2PO_4 , Na_2HPO_4 , and Na_3PO_4 . It is also tribasic, because with silver nitrate its soluble salts always give Ag_3PO_4 ,¹⁵ a salt with three equivalents of

^{14a} The difference between the reactions of ortho-, meta-, and pyro-phosphoric acids, established by Graham, is of such importance for the theory of hydrates and for explaining the nature of solutions, that in my opinion its influence upon chemical thought has been far from exhausted. At the present time many such instances are known both in organic (for instance, the difference between the reactions of the solutions of certain anhydrides and hydrates of acids) and inorganic chemistry (for example, the difference between the rose and purple cobalt compounds, Chap. XXII. &c.). They essentially recall the long known and generalised difference between C_2H_4 (ethylene), $\text{C}_2\text{H}_5\text{O}$ (ethyl alcohol = ethylene + water), and $\text{C}_2\text{H}_5\text{O}$ (ethyl ether = 2 ethylene + water = 2 alcohol - water). The power of meta- and pyro-phosphoric acids to pass gradually into the ortho-acid in the presence of water and the converse transition with the elimination of water show that the differences between them are not so very deep. Experiment (Montemartini, 1902) shows that dilute solutions of the pyro-acid pass into the ortho-acid more slowly than strong solutions, and this apparently indicates that the transition takes place, so to say, without the reaction of the actual molecules of phosphoric acid. The metaphosphoric acid absorbs water more slowly than the pyro-acid. Solutions of the sodium salts are far more stable than those of the acids themselves.

^{14b} Other indicators (Chap. III., note 50) give other results, as Berthelot and others discovered; but I consider that distinctions of this kind throw little light on the essence of the matter, and shall therefore not linger further on them.

¹⁵ Silver orthophosphate, Ag_3PO_4 , is yellow, of sp. gr. 7.32, and insoluble in water. When heated it fuses like silver chloride, and if kept fused for some length of time it gives a white pyrophosphate (the decomposition which causes this is not known). It is soluble in aqueous solutions of phosphoric, nitric or even acetic acid, of ammonia, and of many of its salts. If silver nitrate acts on a dimetallie orthophosphate—for instance, Na_2HPO_4 —it still gives Ag_3PO_4 , nitric acid being disengaged: $\text{Na}_2\text{HPO}_4 + 3\text{AgNO}_3 = \text{Ag}_3\text{PO}_4 + 2\text{NaNO}_3 + \text{HNO}_3$. When alcohol is added to silver orthophosphate Ag_3PO_4 , dissolved in syrupy phosphoric acid, it precipitates a white salt (the alcohol takes up the free phosphoric acid) having the composition Ag_2HPO_4 , which is immediately decomposed by water into the normal salt and phosphoric acid.

silver, and because by double decomposition with barium chloride it forms a salt of the composition $\text{Ba}_3(\text{PO}_4)_2$, and silver and barium hardly ever give basic salts. The monometallic orthophosphates of the metals of the alkalis are slightly soluble in water, but the trimetallic salts, $\text{R}_3(\text{PO}_4)_2$ and even the di-salts $\text{R}_2\text{H}_2(\text{PO}_4)=\text{R}_2(\text{HPO}_4)_2$ are insoluble in water, but dissolve in feeble acids, such as phosphoric and acetic, because they then form soluble acid or monometallic salts, $\text{RH}_4(\text{PO}_4)_2$ or $\text{R}(\text{H}_2\text{PO}_4)_2$.¹⁶

Phosphoric anhydride, or any of its hydrates, when ignited with an excess of sodium hydroxide, carbonate, &c., forms **normal** or **trisodium orthophosphate**, Na_3PO_4 , but when a solution of sodium carbonate is decomposed by orthophosphoric acid, only the salt Na_2HPO_4 is formed; and when an excess of sodium chloride is ignited with orthophosphoric acid, hydrochloric acid is evolved, and the acid salt H_2NaPO_4 alone is formed. These facts^{16a} clearly indicate the small

¹⁶ The researches of Thomsen showed that in very dilute aqueous solutions the majority of monobasic acids—nitric, acetic, hydrochloric, &c. (but hydrofluoric acid more and hydrocyanic less)— HX evolve the following amounts of heat (in thousands of calories) with caustic soda: $\text{NaHO} + 2\text{HX} = 14$; $\text{NaHO} + \text{HX} = 14$; $2\text{NaHO} + \text{HX} = 14$; that is, if n be a whole number, $n\text{NaHO} + \text{HX} = 14$ and $\text{NaHO} + n\text{HX} = 14$. Hence reaction here only takes place between one molecule of NaHO and one molecule of acid, and the remaining quantity of acid or alkali does not enter into the reaction. In the case of dibasic acids, $\text{H}_2\text{R}''$ (sulphuric, dithionic, oxalic, sulphuretted hydrogen, &c.), $\text{NaHO} + 2\text{H}_2\text{R}'' = 14$; $\text{NaHO} + \text{H}_2\text{R}'' = 14$; $2\text{NaHO} + \text{H}_2\text{R}'' = 28$; $n\text{NaHO} + \text{H}_2\text{R}'' = 28$; that is, with an excess of acid ($\text{NaHO} + 2\text{H}'_2\text{R}''$) 14 thousand units of heat are developed, and with an excess of alkali 28. When phosphoric acid is taken (but not all tribasic acids—for instance, not citric), the general character of the phenomenon is similar to the preceding, namely, $\text{NaHO} + 2\text{H}_3\text{PO}_4 = 14.7$; $\text{NaHO} + \text{H}_3\text{PO}_4 = 14.8$; $2\text{NaHO} + \text{H}_3\text{PO}_4 = 27.1$; $3\text{NaHO} + \text{H}_3\text{PO}_4 = 34.0$; $6\text{NaHO} + \text{H}_3\text{PO}_4 = 35.3$; or, in general terms, $\text{NaHO} + n\text{H}_3\text{PO}_4 = 14$ (approximately and $n\text{NaHO} + \text{H}_3\text{PO}_4 = 35$ and not 42, which shows a peculiarity of phosphoric acid, i.e., the third equivalent of hydrogen acts more feebly than the first two. It will be seen from the preceding figures that $\text{H}_3\text{PO}_4 + \text{NaHO} = 14.8$; $\text{NaH}_2\text{PO}_4 + \text{NaHO} = 12.3$; $\text{Na}_2\text{HPO}_4 + \text{NaHO} = 5.9$; with $\text{Na}_3\text{PO}_4 + \text{NaHO}$, a very small amount of heat is evolved, as may be judged from the fact that $\text{Na}_3\text{PO}_4 + 3\text{NaHO} = 1.3$, but still heat is evolved. It must be supposed that in acting on phosphoric acid in the presence of a large quantity of water, a certain portion of the sodium hydroxide remains as alkali uncombined with the acid. Thus, on increasing the mass of the alkali heat is still evolved, and a fresh interchange between Na and H takes place. Hence water shows a decomposing action on the alkali phosphates. Recent researches made by Berthelot and Louguine have confirmed the above deductions made by me in the first edition (1871) of this work. At the present time views of this nature are somewhat generally accepted, although they are not sufficiently strictly applied in other cases. As regards PH_3O_4 it may be said that on the substitution of the first hydrogen this acid acts as a powerful acid (like HCl , HNO , H_2SO_4); on the substitution of the second hydrogen as a weaker acid (like an organic acid); and on the substitution of the third, as one of the weakest acids, for instance, like phenol, HCN , &c.

The trimetallic salts of the tri-equivalent bases (Fe_2O_3 , Al_2O_3 , &c.) of the composition FePO_4 , AlPO_4 , are worthy of attention, because they are distinguished by their comparative stability and extreme simplicity of composition.

^{16a} And also the reactions given by different indicators (Chap. III., note 50), as was shown by Berthelot (see note 14b).

energy of phosphoric acid with respect to the formation of the trimetallic salt, which is seen further from the fact that the salt Na_3PO_4 has an alkaline reaction, decomposes in the presence of water and carbonic acid, forming Na_2HPO_4 , corrodes glass vessels in which it is boiled or evaporated, just like solutions of the alkalies; disengages, like them, ammonia from ammonium chloride, and crystallises from solutions, as $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$, only in the presence of an excess of alkali. At 15° the crystals of this salt require five parts of water for solution; they fuse at 77° .

Disodium orthophosphate, or common sodium phosphate, Na_2HPO_4 , is more stable both in solution and in the solid state. As it is used in medicine and in dyeing, it is prepared in considerable quantities, most frequently from the impure phosphoric acid obtained by the action of sulphuric acid on bone ash. The solution thus formed—which contains, besides phosphoric and sulphuric acids, salts of sodium, calcium, and magnesium—is heated, and sodium carbonate added so long as carbonic anhydride is disengaged. A precipitate is formed containing the insoluble salts of magnesium and calcium, whilst the solution contains sodium phosphate, Na_2HPO_4 , with a small quantity of other salts, from which it may be easily purified by crystallisation. At the ordinary temperature its solutions, especially in the presence of a small amount of sodium carbonate, give well-formed inclined prismatic crystals, $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$; when the crystals are deposited above 30° they only contain $7\text{H}_2\text{O}$. The former crystals even lose a portion of their water of crystallisation at the ordinary temperature (the salt effloresces), and form the second salt with $7\text{H}_2\text{O}$; whilst under the receiver of an air-pump and over sulphuric acid they also part with this water.¹⁷ When ignited they lose the last molecule of water of constitution, and give sodium pyrophosphate, $\text{Na}_4\text{P}_2\text{O}_7$.

Monosodium orthophosphate, NaH_2PO_4 , crystallises with one equivalent of water; its solution has an acid reaction. At 100° the salt loses only this water of crystallisation, but at about 200° it parts with all its water, forming the metaphosphate NaPO_3 . It is prepared from ordinary sodium phosphate by adding phosphoric acid until the

¹⁷ $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ has a sp. gr. 1.53. Poggiale determined the solubility in 100 parts of water (1) of the anhydrous ortho-salt Na_2HPO_4 , and (2) of the corresponding pyro-salt $\text{Na}_4\text{P}_2\text{O}_7$:—

	0°	20°	40°	80°	100°
(1)	1.5	11.1	30.9	81	108
(2)	3.2	6.2	13.5	30	40

At temperatures of 20° to 100° the ortho-salt is so very much less soluble that this difference alone is sufficient to indicate the deeply seated alteration in constitution which takes place in the passage from the ortho- to the pyro-salts.

solution does not give a precipitate with barium chloride, and then evaporating and crystallising the solution. The solution of this salt does not absorb carbonic anhydride, and does not give a precipitate with salts of calcium, barium, &c.¹⁸

¹⁸ The **ammonium orthophosphates** resemble the sodium salts in many respects, but the instability of the di- and tri-metallic salts is seen in them still more clearly than in the sodium salts; thus $(\text{NH}_4)_3\text{PO}_4$, and even $(\text{NH}_4)_2\text{HPO}_4$, lose ammonia in the air (especially when heated, even in solutions); $\text{NH}_4\text{H}_2\text{PO}_4$ alone does not disengage ammonia and has an acid reaction. The crystals of the first salt contain $3\text{H}_2\text{O}$, and are only formed in the presence of an excess of ammonia; both the others are anhydrous, and may be obtained like the sodium salts. When ignited, these salts leave metaphosphoric acid behind; for example, $(\text{NH}_4)_2\text{HPO}_4 = 2\text{NH}_3 + \text{H}_2\text{O} + \text{HPO}_3$. Ammonia also enters into the composition of many double phosphates. **Ammonium sodium orthophosphate**, $\text{NH}_4\text{NaHPO}_4 \cdot 4\text{H}_2\text{O}$, crystallises in large transparent crystals from a mixture of the solutions of disodium phosphate and ammonium chloride (in which case sodium chloride is obtained in the mother liquor), or, better still, from a solution of monosodium phosphate saturated with ammonia. It is also formed from the phosphates in urine when it ferments. This salt is frequently used in testing metallic compounds by the blow-pipe, because when ignited it leaves a vitreous metaphosphate, NaPO_3 , which, like borax, dissolves metallic oxides, forming characteristically tinted glasses.

When a solution of trisodium phosphate is added to a solution of a magnesium salt it gives a white precipitate of the normal orthophosphate, $\text{Mg}_3(\text{PO}_4)_2 \cdot 7\text{H}_2\text{O}$. If the trisodium salt be replaced by the ordinary salt, Na_2HPO_4 , a precipitate is also formed, and $\text{MgHPO}_4 \cdot 7\text{H}_2\text{O}$ is obtained. It might be thought that the normal salt, $\text{Mg}_3(\text{PO}_4)_2$, would be precipitated if disodium phosphate was added to ammonia and a salt of magnesium, but in reality **ammonium magnesium orthophosphate**, $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$, is precipitated as a crystalline powder, which loses ammonia and water when ignited, and gives a pyrophosphate, $\text{Mg}_2\text{P}_2\text{O}_7$. This salt occurs in nature as the mineral *struvite*, and in various products of the changes of animal matter. If we consider that the above salt parts with ammonia with difficulty, and that the corresponding salt of sodium is not formed under the same conditions ($\text{MgNaPO}_4 \cdot 9\text{H}_2\text{O}$ is obtained by the action of magnesia on disodium phosphate), and turn our attention to the fact that the salts of calcium and barium do not form double salts as easily as magnesium, remembering that the salts of magnesium in general easily form double ammonium salts, we are led to think that this salt is not really a normal, but an acid salt, corresponding with Na_2HPO_4 , in which Na_2 is replaced by the equivalent group NH_3Mg .

The common normal **calcium phosphate**, $\text{Ca}_3(\text{PO}_4)_2$, occurs in minerals, in animals, especially in bones, and also probably in plants, although the ash of many portions of plants, as a rule, contains less lime than the formation of the normal salt requires. Thus, 100 parts of the ash (from 5,000 parts of grain) of rye grain contain 47.5 of phosphoric anhydride and only 2.7 of lime, and even the ash of the whole of the rye (including the straw) contains twice as much phosphoric anhydride as lime, and the normal salt contains almost equal weights of these substances. Only the ash of grasses, and especially of clover, and of trees, contains in the majority of cases more lime than is required for the formation of $\text{Ca}_3\text{P}_2\text{O}_8$. This salt, which is insoluble in water, dissolves even in such feeble acids as acetic and sulphurous, and even in water containing carbonic acid. The latter fact is of immense importance in nature, since by reason of it rain water is able to transfer the calcium phosphates in the soil into solutions which are absorbed by plants. The solubility of the normal salt in acids takes place by virtue of the formation of an acid salt, which is evident from the quantity of acid required for its solution, and more especially from the fact that the acid solutions when evaporated give crystalline scales of the acid calcium phosphate, $\text{CaH}_4(\text{PO}_4)_2$, soluble in water. This solubility of the acid salt forms the basis of the treatment by acids of bones, phosphorites, guano, and other natural products containing the normal salt and employed for fertilising the soil. The

As a hydrate, orthophosphoric acid should be expressed, after the fashion of other hydrates, as containing three water residues (hydroxyl groups), i.e., as $\text{PO}(\text{OH})_3$. This method of expression indicates that the type PX_3 , seen in PH_3I , is here preserved, with the substitution of X_2 by oxygen and X_3 by three hydroxyl groups. The same type appears in POCl_3 , PCl_5 , PF_5 , &c. And if we recognise phosphoric acid as $\text{PO}(\text{OH})_3$, we should expect to find three anhydrides corresponding with it: (1) $[\text{PO}(\text{OH})_2]_2\text{O}$, in which two of the three hydroxyls are preserved; this is pyrophosphoric acid, $\text{H}_4\text{P}_2\text{O}_7$. (2) $\text{PO}(\text{OH})\text{O}$, where only one hydroxyl is preserved. This is metaphosphoric acid. (3) $(\text{PO})_2\text{O}_3$ or P_2O_5 , that is, perfect phosphoric anhydride. Therefore, **pyro- and meta-phosphoric acids are imperfect anhydrides (or anhydro-acids) of orthophosphoric acid.**¹⁹

Pyrophosphoric acid, $\text{H}_4\text{P}_2\text{O}_7$, is formed by heating orthophosphoric acid to 250° , when it loses water.^{19a} Its normal salts are formed by igniting the dimetallic salts of orthophosphoric acid of the types HM_2PO_4 . Thus from the disodium salt we obtain sodium pyrophosphate, $\text{Na}_4\text{P}_2\text{O}_7$ (it crystallises from water with $10\text{H}_2\text{O}$, is very complete decomposition requires at least $2\text{H}_2\text{SO}_4$ to $\text{Ca}_3(\text{PO}_4)_2$, but in reality less is taken, so that only a portion of the normal salt is converted into the acid salt. Hydrochloric acid is sometimes used. (In practice such mixtures are known as **superphosphates**.) Certain experiments, however, show that a thorough grinding, the presence of organic, and especially of nitrogenous, substances, and the porous structure of some calcium phosphates (for example, in burnt bones), render the treatment of phosphoric manures by acids superfluous—that is, the crop is not improved by it.

¹⁹ In this sense the ortho-acid itself might be considered as an anhydro-acid, regarding $\text{P}(\text{HO})_3$ as the perfect hydrate, if PH_3 existed; but as, in general, the normal hydrates correspond with the existing hydrogen compounds with the addition of up to 4 atoms of oxygen, PH_3O_4 is the normal acid, just as SH_2O_4 and ClHO_4 are; while NHO_3 , CH_2O_3 are meta-acids, or higher normal acids (NH_3O_4 and CH_4O_4) with the loss of a molecule of water.

In order to see the relation between the ortho-, pyro-, and meta-phosphoric acids, the first thing to remark in them is that the anhydride P_2O_5 is combined with 3, 2, and 1 molecules of water. In the absence of data for the molecular weight of ortho- and pyrophosphoric acids it is necessary to mention that all existing data for meta-phosphoric acid indicate (note 21) that its molecule is much more complex and contains at least $\text{H}_3\text{P}_3\text{O}_9$ or $\text{H}_6\text{P}_3\text{O}_{18}$. The explanation of the problems which here present themselves can, it seems to me, be only looked for after a detailed study of the phenomena of the polymerisation of mineral substances, and of those complex acids, such as phosphomolybdic, which we shall hereafter describe (Chap. XXI.). A similar instance is exhibited in the solubility of hydrate of silica (produced by the action of silicon fluoride on water) in fused metaphosphoric acid, with the formation, on cooling, of an octahedral compound (sp. gr. 3.1) of the composition $\text{SiO}_2\cdot\text{P}_2\text{O}_5$. A certain indication (but no proof) that ordinary orthophosphoric acid is polymerised is given by Staudenmaier (1893), who obtained a salt, $\text{K}_5\text{H}_1\text{P}_3\text{O}_{12}$, by the action of a solution of KH_2PO_4 upon K_2CO_3 , and a compound, $\text{KH}_3\text{P}_2\text{O}_8$, corresponding to the doubled molecule of H_3PO_4 , by the action of KH_2PO_4 upon H_3PO_4 itself.

^{19a} According to Watson (1893) the ortho-acid is partially transformed into the pyro-acid at 230° , whilst at 260° the latter begins to volatilise. At 300° the meta-acid only is formed.

stable, fuses when heated, and has an alkaline reaction ;^{19b} and the monosodium salt, NaH_2PO_4 , yields the acid salt, $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$ (easily soluble in water), which has an acid reaction, and when ignited further gives the meta-salt.²⁰

Metaphosphoric acid, HPO_3 (the analogue of nitric acid), is formed by the ignition of the pyro- and ortho-acids (or, better, of their ammonium salts), as a vitreous, hygroscopic, fused mass (*glacial phosphoric acid*, *acidum phosphoricum glaciale*), soluble in water and volatilising without decomposition. It is also formed in the first slow action of cold water on the anhydride, but metaphosphoric acid gradually changes into the ortho-acid when its solution is boiled, or when it is kept for any length of time, especially in the presence of acids.²¹

^{19b} Solutions of the pyro-acid gradually, but very slowly, pass into the ortho-acid if kept at the ordinary temperature; the first day about 5 per cent. of the acid is converted into ortho-acid, then the conversion proceeds still more slowly, so that after the course of three months only about half the acid is converted. The presence of acids and also heating facilitate the conversion. The neutral sodium salt is more stable than the acid, and its solutions do not change on (prolonged ?) boiling.

²⁰ The method of preparation of the acid itself consists in converting the sodium salt, $\text{Na}_4\text{P}_2\text{O}_7$, by double decomposition with water and a salt of lead, into insoluble lead pyrophosphate, $\text{Pb}_2\text{P}_2\text{O}_7$, which is then suspended in water and decomposed by sulphuretted hydrogen; lead sulphide is thus precipitated, and pyrophosphoric acid remains in solution. The solution is evaporated under the receiver of an air-pump. It concentrates to a syrup and crystallises, and when ignited in this form loses water and forms metaphosphoric acid. It resembles orthophosphoric acid in many respects; its salts with the alkalis are also soluble, and the others insoluble in water but soluble in acids. When heated in solution with acid it gives orthophosphoric acid, as well as when fused with an excess of alkali.

Witt heated ammonium chloride with phosphoric acid (hydrochloric acid was evolved), ignited the residue to drive off ammonia, and obtained pyrophosphoric acid in the residue.

²¹ As, when using phenolphthalein as an indicator in neutralising with an alkali, metaphosphoric acid is monobasic, and orthophosphoric acid dibasic, it is possible by means of this difference to follow the transition of meta- into ortho-phosphoric acid. Sabatier (1888) carried on an investigation of this nature, and found that the rate of transformation is dependent on the temperature, and is subject to the general laws of the rate of chemical transformations which belong to physical chemistry.

Metaphosphoric acid has a particular interest in respect to the variations to which its salts are subject. The metaphosphates are formed by the ignition of the acid orthophosphates, MH_2PO_4 , or MNH_4HPO_4 , or of the acid pyrophosphates, $\text{M}_2\text{H}_2\text{P}_2\text{O}_7$, or $\text{M}_2(\text{NH}_4)_2\text{P}_2\text{O}_7$, water and ammonia being given off in the process. The properties of the metaphosphates, which have a similar composition to nitrates—for instance, NaPO_3 , or $\text{Ba}(\text{PO}_3)_2$ —vary according to the duration of the ignition to which the ortho-, or pyrophosphates from which they are prepared have been subjected. When the salts NaH_2PO_4 or $\text{NH}_4\text{NaHPO}_4$ are strongly ignited, a salt, NaPO_3 , is formed, which deliquesces in the air, and gives a gelatinous precipitate with salts of the alkaline earths. But, as Graham (in 1830-40), and many others, especially Fleitmann and Hanneberg (in 1840-50), and Tammann (in the nineties), observed, under other conditions the salts of the same composition acquire other properties. The above chemists recognise five polymeric forms of metaphosphates, $(\text{HPO}_3)_n$. We shall follow the nomenclature and researches of Fleitmann.

Monometaphosphoric acid. The salts are distinguished for their insolubility in

In order to see the relation between phosphoric acid and the lower acids of phosphorus, it is simplest to imagine the substitution of hydroxyl in H_3PO_4 or $\text{PO}(\text{OH})_3$ by hydrogen. Then from orthophosphoric acid, $\text{PO}(\text{OH})_3$ we shall obtain phosphorous acid, $\text{POH}(\text{OH})_2$, and hypophosphoric acid, $\text{POH}(\text{OH})$; and, furthermore, phosphorous acid should be dibasic if orthophosphoric acid is tribasic, and hypophosphorous acid should be monobasic. This conclusion ^{21a} is, in

water; even the salts NaPO_3 , KPO_3 , are insoluble. They are obtained by igniting the monometallic orthophosphates—for example, RH_2PO_4 —up to the temperature at which all water is evolved (316°), but not to fusion. No double salts are known.

Dimetaphosphoric acid, on the contrary, easily forms double salts—for example, KNaP_2O_6 , and also the copper potassium salt, &c. The copper salt is obtained by evaporating a solution of copper oxide in orthophosphoric acid. A blue ortho-salt, CuRHO_4 , first separates from the solution, then a light-blue pyro-salt, $\text{Cu}_2\text{P}_2\text{O}_7$; and above 350° , when metaphosphoric acid itself begins to volatilise, the dimetaphosphate, CuP_2O_6 , is formed. The residue is washed with water, and decomposed with a hot solution of sodium sulphide, when the sodium salt, $\text{Na}_2\text{P}_2\text{O}_6$, is obtained in solution. This salt, when evaporated with alcohol, gives crystals which contain 2 mols. of H_2O , but retain their solubility (in 7 parts of water) after the water is driven off at 100° . When fused, these crystals give a deliquescent salt (hexa-metaphosphate). The solution of the salt has a neutral reaction, which only after prolonged boiling becomes acid, owing to the formation of orthophosphate, NaH_2PO_4 . The soluble salts of dimetaphosphoric acid give the insoluble silver salt, $\text{Ag}_2\text{P}_2\text{O}_6$, with silver nitrate, and a precipitate of $\text{BaP}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$ with barium chloride.

Trimetaphosphoric acid is obtained as the sodium salt, $\text{Na}_3\text{P}_3\text{O}_9$, when any other metaphosphate of sodium is fused and *slowly* cooled, then dissolved in a slight excess of warm water, and the resultant solution evaporated. The crystals contain 6 mols. H_2O , and dissolve in four parts of water. An acid reaction is only obtained, as with the preceding salt, after prolonged boiling with water. The acid is a true analogue of nitric acid, because *all its metallic salts are soluble*.

Hexametaphosphoric acid. Fleitmann so named the ordinary metaphosphoric acid (glacial) which attracts moisture. The deliquescent sodium salt is obtained like the trimetaphosphate, only by *rapid* cooling. It is also formed by fusing silver oxide with an excess of phosphoric acid. The sodium salt is soluble in water, and gives viscous, elastic precipitates with salts of Ba, Ca, and Mg. Lubert (1893) obtained salts of Ag, Pb, &c.

Jawcin and Thillot (1889), who investigated the sodium salts of metaphosphoric acid by Raoult's method, came to the conclusion that the salts of di- and tri-metaphosphoric acid behave in such a manner that their molecule must be represented as non-polymerised, NaPO_3 , whilst those of hexametaphosphoric acid behave as $(\text{NaPO}_3)_4$. At all events the series of salts which Fleitmann and Henneberg regard as monometaphosphates—i.e., as non-polymerised—are most probably the most polymerised, because they are insoluble.

According to Tammann's researches, vitreous metaphosphoric acid contains a mixture consisting chiefly of two varieties, differing in the solubility and degree of stability of their salts. The least stable corresponds to Fleitmann's hexa-acid, and gives three isomeric salts. Tammann came to the conclusion that there exist polymers also in the form of penta-, octo-, and deca-metaphosphoric acids. Without going into details upon this subject, I do not think it superfluous to point out that the degree of polymerisation and the number of polymeric forms cannot yet be considered as sufficiently explained.

^{21a} The dibasity of H_3PO_3 , established by Würtz, has been proved by many direct experiments (see, for instance, note 22), among which we may mention that Amat (1892)

fact, true, and hence all the acids of phosphorus may be referred to one common type, PX_5 , whose representatives are PH_4I and Cl_5 , $POCl_3P$, PCl_2F_3 , &c.

Phosphorous acid, PH_3O_3 , is generally obtained from phosphorus trichloride, PCl_3 , by the action of water: $PCl_3 + 3H_2O = 3HCl + PH_3O_3$. Both acids formed are soluble in water, but are easily separated, because hydrochloric acid is volatile whilst phosphorous acid volatilises with difficulty, and if a small amount of water is originally taken the hydrochloric acid nearly all passes off directly. Concentrated solutions of phosphorous acid give crystals of H_3PO_3 , which fuse at 70° , attract moisture from the air, and deliquesce when ignited, giving phosphine and phosphoric acid,²² and are converted into orthophosphoric acid by many oxidising agents. In its salts only two hydrogen atoms are replaced by metals (Würtz); the salts of the alkaline metals are soluble, and give precipitates with the salts of the majority of other metals.

took a mixture of the aqueous solutions of Na_2HPO_3 and $NaHO$ and added absolute alcohol to it. Two layers were formed; the upper, alcoholic one, contained all the excess of $NaHO$, whilst the lower only contained the salt Na_2HPO_3 , which was therefore unable to react with the excess of $NaHO$. Amat also obtained NaH_2PO_3 by saturating H_3PO_3 with soda until he obtained a neutral reaction with methyl-orange. The replacement of one atom of H by sodium here, as in phosphoric acid (note 16), gives more heat than the replacement of the second atom. For the third atom there is no formation of a salt, and therefore no evolution of heat. The monometallic salts—for example, NaH_2PO_3 —or the ammonium salts, when heated to 160° , give, as Amat had previously shown, a salt of dibasic pyrophosphorous acid, $Na_2H_2P_2O_5$.

²² Phosphorous acid, when subjected to the action of nascent hydrogen (zinc and sulphuric acid), evolves phosphine, and when boiled with an excess of alkali it yields hydrogen ($PH_3O_3 + 3KHO = PK_3O_4 + 2H_2O + H_2$); owing to its liability to oxidation, it is a reducing agent—for instance, it reduces cupric chloride to cuprous chloride, and precipitates silver from the nitrate and mercury from its salts.

These reactions are connected with the fact that in this acid one atom of hydrogen should be considered as in the same condition as in phosphoretted hydrogen, which is expressed by the formula $PHO(OH)_2$, if we represent it as PH_4X , with the substitution of two of the hydrogen atoms by oxygen and of HX by two of hydroxyl. The direct passage of phosphorous chloride into phosphorous acid would, however, indicate that all three atoms of hydrogen in it occur in the form of hydroxyl, because no difference is known between the three atoms of chlorine in PCl_3 —they all react alike, as a rule. However, Menshutkin, by acting on alcohol, C_2H_5OH , with phosphorous chloride, obtained hydrochloric acid and a substance $P(C_2H_5O)Cl_2$, and from this by the action of bromine he obtained ethyl bromide, C_2H_5Br , and a compound $PBrOCl_2$, which proves, to a certain extent, the existence of a difference between the three atoms of hydrogen in PH_3O_3 . If we turn our attention to the formation of phosphine by the ignition of phosphorous acid, we see that $4PH_3O_3$ only evolves $3H$ in the form of PH_3 , and therefore the residue—that is, $3PH_3O_4$ —will still contain one hydrogen of the same nature as in phosphine, because in $4PH_3O_3$ we shall recognise four such hydrogens as in phosphine. We arrive at the same conclusion by examining the decomposition of hypophosphorous acid, $2PH_3O_2 = PH_3 + PH_3O_4$. In the two molecules of the monobasic hypophosphorous acid taken, there are only two atoms of hydrogen replaceable by metals, whilst in the molecule of the resultant phosphoric acid there are three. Perhaps relations of this nature determine the relative stability of the di-metallic salts of orthophosphoric acid.

The monobasic **hypophosphorous acid**, PH_3O_2 , gives salts $\text{PH}_2\text{O}_2\text{Na}$, $\text{PH}_2\text{O}_2)_2\text{Ba}$, &c.; the two remaining atoms of hydrogen (which exist in the same form as in phosphine, PH_3) are not replaceable by metals, and this determines the property of these salts of evolving phosphoretted hydrogen when heated (especially with alkalies). In acting on substances liable to reduction it is this hydrogen which acts, and, for example, **reduces** gold and mercury from the solutions of their salts, or converts cupric into cuprous salts. In all these instances the hypophosphorous acid is converted into phosphoric acid. Under the action of zinc and sulphuric acid it gives phosphine, PH_3 . Nevertheless, neither hypophosphorous acid nor its dry salts absorb oxygen from the air. The salts of hypophosphorous acid are more soluble than those of the preceding acids of phosphorus. Thus the sodium salt PNaH_2O_2 does not give a precipitate with barium chloride, and the salts of calcium, barium, and many other metals are soluble.²³ The hypophosphites are prepared by boiling an alkali with phosphorus as long as phosphoretted hydrogen is evolved. The acid itself is obtained from barium hypophosphite (prepared in the same manner by boiling phosphorus in baryta water), by decomposing its solution with sulphuric acid. By concentration of the solution of hypophosphorous acid (it must not be heated above 130° , at which temperature it decomposes), a syrup is formed which is able to crystallise. In the solid state hypophosphorous acid fuses at $+17^\circ$, and has the properties of a clearly defined acid.

The types PX_3 and PX_5 , which are evident for the hydrogen and oxygen compounds of phosphorus, are most clearly seen in its halogen compounds,²⁴ to the consideration of which we shall now proceed, fixing our attention more especially on the chlorine compounds, as being the most important from the historical, theoretical, and practical points of view.

²³ Calcium hypophosphite is used in medicine. According to Cavazzi, a mixture of sodium hypophosphite, NaH_2PO_2 , and sodium nitrate explodes violently.

²⁴ Fluorine and bromine give PX_3 and PX_5 , like chlorine. With respect to iodine, PI_5 is, in a chemical sense, a very unstable substance, and generally **phosphorus tri-iodide** only is formed (from yellow or red phosphorus and iodine in the requisite proportions). It is a red crystalline substance, fuses at 55° , is easily decomposed by water, forming phosphorous and hydriodic acids, and when heated, it evolves iodine vapours and forms **phosphorus di-iodide**, PI_2 . This substance may be obtained in the same manner as the preceding by taking a smaller proportion of iodine (8 parts of iodine to 1 part of phosphorus, whilst the tri-iodide requires 12.3); it also forms red crystals, which melt at 110° . When decomposed by water it gives not only phosphorous and hydriodic acids, but also phosphine and a yellow substance (a lower oxide of phosphorus). In its composition, di-iodide of phosphorus corresponds with liquid phosphoretted hydrogen, PH_2 , but probably its molecular weight is much higher: P_2I_4 or P_3I_6 , &c. As the iodine compounds of phosphorus give hydriodic and phosphorous acids with water, and as both these substances are reducing agents in the presence of water (and hydrates), iodide of phosphorus also acts as a reducing agent.

Phosphorus burns in chlorine, forming phosphorous chloride, PCl_3 , and with an excess of chlorine, phosphoric chloride, PCl_5 . The oxychloride, POCl_3 , as the simplest chloranhydride according to the type PX_5 , and also phosphoric chloride, correspond with orthophosphoric acid, $\text{PO}(\text{OH})_3$, while phosphorous chloride, PCl_3 , corresponds with phosphorous acid and the type PX_3 . **Phosphorus oxychloride**, POCl_3 , is a colourless liquid, boiling at 110° . Phosphorus trichloride is also a colourless liquid, boiling at 76° ,²⁵ whilst phosphoric chloride

²⁵ In a liquid state the density of phosphorous chloride at 10° is 1.597, and therefore its molecular volume = $137.5/1.597 = 86.0$, and that of phosphorus oxychloride is equal to $153.5/1.693 = 90.7$; hence the addition of oxygen has produced considerable increase in volume, just as in the conversion of sulphur dichloride, SCl_2 , into sulphuryl chloride, SOCl_2 , the volume changes from 64 to 71. It is the same with the boiling-points; phosphorus trichloride boils at 70° , the oxychloride at 100° , sulphur dichloride at 64° , and sulphuryl chloride at 78° —that is, the addition of oxygen raises the boiling-points.

The vapour densities of phosphorus trichloride and oxychloride correspond with their formulæ (Cahours, Würtz), being equal to half the molecular weight referred to hydrogen. But it is not so with phosphorus pentachloride. Cahours showed that the vapour density of phosphorus pentachloride referred to air is 3.65, or to hydrogen, 52.6, whilst according to the formula PCl_5 it should be 104.2. Hence this formula corresponds with four, and not with two, molecules. This shows that the vapour of phosphoric chloride contains two molecules and not one, so that in a state of vapour it splits up, like sal-ammoniac, sulphuric acid, &c. The products of disruption must here be phosphorous chloride, PCl_3 , and chlorine, Cl_2 , bodies which easily re-form phosphoric chloride, PCl_5 , at a lower temperature. This decomposition of phosphoric chloride in its conversion into vapour is confirmed by the fact that the vapour of this almost colourless substance shows the greenish-yellow colour peculiar to chlorine. This dissociation of phosphoric chloride has been considered by some chemists as a sign that phosphorus, like nitrogen, does not give volatile compounds of the type PX_5 , and that such substances are only obtained as unstable molecular compounds which break up when distilled: for example, PH_3 , HI ; PCl_3 , Cl_2 ; NH_3 , HCl ; &c. To prove that the molecule PCl_5 actually exists, Würtz in 1870 showed that when mixed with the vapour of phosphorous chloride the vapour of phosphoric chloride is (from 160° to 190°) perfectly colourless, and has a density which is really near to that required by the formula—namely, to 104—and the same density was determined for the pentachloride in an atmosphere of chlorine. Hence, at low temperatures and in admixture with one of the products of dissociation, there is no longer that decomposition which occurs at higher temperatures—that is, we have here a case of dissociation proceeding at moderate temperatures.

An important proof in favour of the type PX_5 is exhibited by **phosphorus pentafluoride**, PF_5 , obtained by Thorpe as a colourless gas which only corrodes glass after the lapse of time; it may be kept over mercury, and has a normal density. It is formed when liquid arsenic trifluoride, AsF_3 , is added to phosphoric chloride surrounded by a freezing mixture: $3\text{PCl}_5 + 5\text{AsF}_3 = 3\text{PF}_5 + 5\text{AsCl}_3$.

In general, fluorine and phosphorus give stable compounds: PF_3 , POF_3 , and PF_5 , as would be expected from the fact that in passing from Cl to I (i.e., as the atomic weight of the halogen increases) the stability of the compounds with P and the tendency to give PX_5 (note 24) decrease. **Phosphorus trifluoride** is obtained by heating a mixture of ZnF_2 and PBr_3 by the action of AsF_3 upon PCl_3 , by heating phosphide of copper with PbF_2 , &c. It is a strong-smelling gas, which liquefies at -10° under a pressure of 40 atmospheres, giving a colourless liquid. It dissolves easily in (is absorbed by, reacts with) water, and acts upon glass; when mixed with Cl_2 it combines with it (Poulenc, 1891), forming $\text{P}(\text{Cl}_2\text{F})_3$, a colourless gas of normal density, which is transformed into a liquid at 8° , decomposes into $\text{PF}_3 + \text{Cl}_2$ at 250° , and, with a small amount

is a solid yellowish substance, which volatilises without melting at about 168° . They are all heavier than water, and form types of the **chloranhydrides** or chlorine compounds of the non-metallic elements whose hydroxides are acids, just as NaCl and BaCl_2 are types of halogen metallic salts.

If a piece of phosphorus is dropped into a flask containing chlorine, it burns when touched with a red-hot wire, and combines with the chlorine. If the phosphorus is in excess, liquid **phosphorus trichloride**, PCl_3 , is always formed, but if the chlorine is in excess the solid pentachloride is obtained. The trichloride is prepared in the following manner. Dry chlorine (passed through a series of Woulfe's bottles containing sulphuric acid) is led into a retort containing sand and phosphorus. The retort is heated, the phosphorus melts, spreads through the sand, and gradually forms the trichloride, which distils over into a receiver, where it condenses. **Phosphoric chloride** or **phosphorus pentachloride**, PCl_5 , is prepared by passing dry chlorine into a vessel containing phosphorus trichloride (purified by distillation). Phosphorous chloride combines directly with oxygen, but more rapidly with ozone or with the oxygen of potassium chlorate ($3\text{PCl}_3 + \text{KClO}_3 = 3\text{POCl}_3 + \text{KCl}$), forming **phosphorus oxychloride**, POCl_3 (Brodie). This compound is also formed by the first action of water on phosphoric chloride; for example, if two vessels, one containing phosphoric chloride and the other water, are placed under a bell-jar, after a certain time the crystals of the chloride disappear and hydrochloric acid passes into the water. The aqueous vapour acts on the pentachloride: $\text{PCl}_5 + \text{H}_2\text{O} = \text{POCl}_3 + 2\text{HCl}$, the result being that liquid phosphorus oxychloride is found in one vessel and a solution of hydrochloric acid in the other. However, an excess of water directly transforms phosphoric chloride into orthophosphoric acid, $\text{PCl}_5 + 4\text{H}_2\text{O} = \text{PH}_3\text{O}_4 + 5\text{HCl}$,²⁶ since POCl_3 reacts with water ($3\text{H}_2\text{O}$), forming 3HCl and phosphoric acid, $\text{PO}(\text{OH})_3$.

of water, gives **oxy-fluoride of phosphorus**, POF_3 (with a large amount of water it gives PH_3O_4), which Moissan (1891) obtained by the action of dry HF upon P_2O_5 , and Thorpe and Tutton (1890) by heating a mixture of cryolite and P_2O_5 . It is a gas of normal density, like PF_3 , and was obtained by Moissan by the action of fluorine upon PF_3 . Thus, the forms PX_3 and PX_5 not only exist in many solid and non-volatile substances, but also as vapours (PSF_3 ; see Chap. XX., note 20).

²⁶ Phosphorus oxychloride is obtained by the action of phosphoric chloride on hydrates of acids (because alkalis decompose phosphorus oxychloride), according to the equation, $\text{PCl}_5 + \text{RHO} = \text{POCl}_3 + \text{RCl} + \text{HCl}$, where RHO is an acid. The reaction only proceeds according to this equation with monobasic acids, but then RCl is volatile, and therefore a mixture is obtained of two volatile substances, the acid chloride and phosphorus oxychloride, which are sometimes difficult to separate; whilst if the hydrate be polybasic, the reaction frequently proceeds so that an anhydride is formed: $\text{RH}_2\text{O}_2 + \text{PCl}_5 = \text{RO} + \text{POCl}_3 + 2\text{HCl}$. If the anhydride be non-volatile (like boric), or

The above chlorine compounds serve not only as a type of the chloranhydrides, but also as a means for the preparation of other **acid chloranhydrides**. Thus the conversion of acids XHO into chloranhydrides, XCl , is generally accomplished by means of phosphorus pentachloride. This fact was discovered by Chancel, and adopted by Gerhardt as an important method for studying organic acids. By this means organic acids, containing, as we know, $RCOOH$ (where R is a hydrocarbon group, and where carboxyl may repeat itself several times by replacing the hydrogen of hydrocarbon compounds), are converted into their chloranhydrides, $RCOCl$. With water they again form the acid, and resemble the chloranhydrides of mineral acids in their general properties.

Since carbonic acid, $CO(OH)_2$, contains two hydroxyl groups, its perfect chloranhydride, $COCl_2$, **carbonic oxychloride**, **carbonyl chloride** or **phosgene gas**, contains two atoms of chlorine, and differs from the chloranhydrides of organic acids in that in them one atom of chlorine is replaced by the hydrocarbon radicle, $RCOCl$, if R be a monatomic radicle giving a hydrocarbon RH . It is evident, on the one hand, that in $RCOCl$ the hydrogen is replaced by the radicle $COCl$, which is also able to replace several atoms of hydrogen (for example, $C_2H_4(COCl)_2$ corresponds with the bibasic succinic acid); and, on the other hand, that the reactions of the chloranhydrides of organic acids will answer to the reactions of carbonyl chloride, as the reactions of the acids themselves answer to those of carbonic acid. Carbonyl chloride is obtained directly from dry carbon monoxide and chlorine ²⁷

easily decomposed (like oxalic), it is easy to obtain pure oxychloride. Thus, phosphorus oxychloride is often prepared by acting on boric or oxalic acid with phosphoric chloride. It is also formed when the vapour of phosphoric chloride is passed over phosphoric anhydride, $P_2O_5 + 3PCl_5 = 5POCl_3$. This forms an excellent example in proof of the fact that the formation of one substance from two does not necessarily show that the resultant compound contains the molecules of these substances in its molecule. But other oxychlorides of phosphorus are also formed by the interaction of phosphoric anhydride and chloride; thus at 200° , PO_2Cl , or chloranhydride of metaphosphoric acid, is formed (Gustavson). The chloranhydride of pyrophosphoric acid, $P_2O_3Cl_4$, was obtained (Hayter and Michaelis), together with $NOCl$, &c., by the action of NO upon cold PCl_3 , as a fuming liquid boiling at 210° .

²⁷ The direct action of the sun's rays, or of magnesium light, is necessary to start the reaction between carbonic oxide and chlorine, but when once started it will proceed rapidly in diffused light. An excess of chlorine (which gives its coloration to the colourless phosgene) aids the completion of the reaction, and may afterwards be removed by metallic antimony. Porous substances, like charcoal, aid the reaction. Phosgene may be prepared by passing a mixture of carbonic anhydride and chlorine over incandescent charcoal. Lead chloride or silver chloride, when heated in a current of carbonic oxide, also partially forms phosgene gas. Carbon tetrachloride, CCl_4 , also forms it when heated with carbonic anhydride (at 400°), with phosphoric anhydride (200°), and most easily of all with sulphuric anhydride ($2SO_3 + CCl_4 = COCl_2 + S_2O_5Cl_2$, this is pyrosulphuryl chloride). Chloroform, $CHCl_3$, is converted into carbonyl chloride when heated

exposed to the action of light, and forms a colourless gas, which easily condenses into a liquid, boiling at $+8^{\circ}$, specific gravity 1.43, and having the suffocating odour belonging to all chloranhydrides. Like all chloranhydrides, it is immediately decomposed by water, forming carbonic anhydride, according to the equation, $\text{COCl}_2 + \text{H}_2\text{O} = \text{CO}_2 + 2\text{HCl}$, and thus expresses the type proper to all chloranhydrides of both mineral and organic acids.²⁸

In order to show the general method for the preparation of acid chloranhydrides, we will take that of acetic acid, $\text{CH}_3\cdot\text{COOH}$, as an example. Phosphorus pentachloride is placed in a glass retort, and acetic acid poured over it; hydrochloric acid is then evolved, and the substance distilling over directly after is a very volatile liquid, boiling at 50° , and having all the properties of the chloranhydrides. With water it forms hydrochloric and acetic acids. The resultant oxychloride boils at 110° , and may therefore be easily separated. The general scheme for the reaction of phosphorus pentachloride with hydrates ROH is exactly the same as with water; namely, ROH with PCl_5 gives $\text{POCl}_3 + \text{HCl} + \text{RCl}$ —that is, a chloranhydride, in this case CH_3COCl .^{28a}

with $\text{SO}_2(\text{OH})\text{Cl}$ (the first chloranhydride of sulphuric acid); $\text{CHCl}_3 + \text{SO}_3\text{HCl} = \text{COCl}_2 + \text{SO}_2 + 2\text{HCl}$ (Dewar), and when oxidised by chromic acid. Among the reactions of phosgene we may mention the formation of urea with ammonia, and of carbonic oxide when heated with metals.

²⁸ We are already acquainted with some of the chloranhydrides of the inorganic acids—for instance, BCl_3 and SiCl_4 —and we shall describe those which correspond with sulphuric acid in the following chapter. It may be mentioned here that, when hydrochloric acts on nitric acid (Aqua Regia, Chap. XI.), there is formed, besides chlorine, the oxychlorides NOCl and NO_2Cl , which may be regarded as **chloranhydrides of nitric and nitrous acids**. The former boils at -5° , the latter at $+5^{\circ}$; the specific gravity of the first at -12° is 1.416, and at -18° , 1.433 (Geuther), and that of the second, 1.3; the first is obtained from nitric oxide and chlorine, the second from nitric peroxide and chlorine, and also by the action of phosphoric chloride on nitric acid. If the gases evolved by aqua regia are passed into cold strong sulphuric acid, they form crystals of the composition NHSO_3 (like chamber crystals), which melt at 86° , and with sodium chloride form acid sodium sulphate and the oxychloride NOCl . This chloranhydride of nitric acid is termed **nitrosyl chloride**.

Cyanogen chloride, CNCl , is the gaseous chloranhydride of cyanic acid; it is formed by the action of chlorine on aqueous mercury cyanide, $\text{Hg}(\text{CN})_2 + 2\text{Cl}_2 = \text{HgCl}_2 + 2\text{CNCl}$. When chlorine acts on cyanic acid, it forms not only this cyanogen chloride, but also polymerides of it—a liquid, boiling at 18° , and a solid, boiling at 190° . The latter corresponds with cyanuric acid, and consequently has the composition $\text{C}_3\text{N}_3\text{Cl}_3$. Details concerning these substances must be looked for in works on organic chemistry.

^{28a} This reaction, indeed, proceeds very easily and completely with a number of hydroxides, if they do not react on hydrochloric acid and phosphorus oxychloride, which is the case when they have alkaline properties. When the hydroxide is dibasic and is present in excess, it not infrequently happens that the elements of water are taken up: $\text{R}(\text{OH})_2 + \text{PCl}_5 = \text{RO} + 2\text{HCl} + \text{POCl}_3$. The anhydride RO may then be converted into chloranhydride, $\text{RO} + \text{PCl}_5 = \text{RCl}_2 + \text{POCl}_3$.

Phosphorus trichloride and oxychloride act in a similar manner to phosphoric chloride. When phosphorus trichloride acts on an acid, $3\text{RHO} + \text{PCl}_3 = 3\text{RCl} + \text{P}(\text{HO})_3$. If a salt

Containing, as they do, chlorine, which easily reacts with hydrogen, phosphorus pentachloride, trichloride, and oxychloride enter into reaction with ammonia, and give a series of amide and nitrile compounds of phosphorus. Among these a **mono-amido-orthophosphoric acid**, $\text{PO}(\text{NH}_2)(\text{OH})_2$ was obtained by Stokes by saponifying the phenol ether, $\text{PO}(\text{NH}_2)(\text{OC}_6\text{H}_5)_2$, formed from POCl_3 and $\text{C}_6\text{H}_5\text{OH}$ after treating the resultant $\text{POCl}(\text{OC}_6\text{H}_5)_2$ with ammonia. An alkaline salt is produced by the saponification and is first converted into a lead salt, and then into the amido-orthophosphoric acid. It is soluble in water but not in alcohol, and forms, as would be expected, both acid and neutral salts, i.e., mono- and di-metallic, but the former give a neutral reaction with litmus, as would be expected from the example of orthophosphoric acid itself. Schiffer, by acting on POCl_3 with ammonia, obtained sal-ammoniac (which is afterwards removed by water) and an orthophosphoric triamide, $\text{PO}(\text{NH}_2)_3$, as a white insoluble powder on which dilute acids and alkalies do not act, but which, when fused with potassium hydroxide, gives potassium phosphate and ammonia like other amides. When ignited, the resultant triamide (its preparation under these conditions has been repeatedly denied) liberates ammonia and forms the nitrile PON , just as urea, $\text{CO}(\text{NH}_2)_2$, gives off ammonia and forms the nitrile CONH . This nitrile, sometimes called **monophosphamide**, although it is undoubtedly the **nitrile** of metaphosphoric acid, corresponds with metaphosphoric acid, namely, with its ammonium salt: $\text{NH}_4\text{PO}_3 - 2\text{H}_2\text{O} = \text{PON}$. This relation is confirmed by the fact that PON , moistened with water, gives metaphosphoric acid when ignited and K_3PO_4 when fused with KHO . It is the analogue of nitrous oxide, NON . It is a very stable compound, colourless, and probably a polymeride.²⁹

is taken, then by the action of phosphorus oxychloride a corresponding chloranhydride and salt of orthophosphoric acid are easily formed: $3\text{R}(\text{KO}) + \text{POCl}_3 = 3\text{RCl} + \text{PO}(\text{KO})_3$. The chloranhydride RCl is always more volatile than its corresponding acid, and distils over before the hydrate RHO . Thus acetic acid boils at 117° , and its chloranhydride at 50° . A chloranhydride RCl is frequently employed for the formation of other compounds of a given radicle R ; for instance, with ammonia they form amides RNH_2 , and with salts ROK , with anhydrides R_2O , &c.

²⁹ The reaction of ammonia on phosphorus pentachloride is more complex than the preceding. This is readily understood: to the oxychloride, POCl_3 , there corresponds a hydrate $\text{PO}(\text{OH})_3$ and a salt $\text{PO}(\text{NH}_4\text{O})_3$ and consequently also an amide $\text{PO}(\text{NH}_2)_3$, whilst the pentachloride, PCl_5 , has no corresponding hydrate $\text{P}(\text{OH})_5$, and therefore there is no amide $\text{P}(\text{NH}_2)_5$. The reaction with ammonia will be of two kinds: either instead of 5 mols. of NH_3 , only 3 mols. or still less will act, i.e., $\text{PCl}_2(\text{NH}_2)_3$, $\text{PCl}_3(\text{NH}_2)_2$, &c., are formed; or else the pentachloride will act like a mixture of chlorine with the trichloride, and then as the result there will be obtained the products of the action of chlorine on those amides which are formed from phosphorus trichloride and ammonia. It would appear that both kinds of reaction proceed simultaneously, but both kinds of products are unstable, at all events complex, and in the result there is obtained a mixture containing

The nearest analogue of phosphorus is **arsenic**, the metallic aspect of which and, what is far more important, the general character of

sal-ammoniac, &c. The products of the first kind should react with water, and we should obtain, for example, $\text{PCl}_3(\text{NH}_2)_2 + 2\text{H}_2\text{O} = 3\text{HCl}$ and $\text{PO}(\text{HO})(\text{NH}_2)_2$. This substance has actually been obtained in a crystalline form, and the compound $\text{PONH}(\text{NH}_2)$ derived from it by elimination of the elements of water is known, and is termed **diphosphamide**: it is, however, more probable that it is a nitrile than an amide, because only amides contain the group NH_2 . It is a colourless, stable, insoluble powder, which possibly corresponds with pyrophosphoric acid, more especially since, when heated, it evolves ammonia and gives phosphoryl nitride, PON —that is, the nitrile of metaphosphoric acid. The amide corresponding with the pyrophosphate, $\text{P}_2\text{O}_3(\text{NH}_4\text{O})_4$, should be $\text{P}_2\text{O}_3(\text{NH}_2)_4$, and the nitriles corresponding to the latter would be $\text{P}_2\text{O}_2\text{N}(\text{NH}_2)_3$, $\text{P}_2\text{ON}_2(\text{NH}_2)_2$, and $\text{P}_2\text{N}_3(\text{NH}_2)$. The composition of the first is the same as that of the above diphosphamide. The third pyrophosphoric nitrile has a formula $\text{P}_2\text{N}_4\text{H}_2$, and this is the composition of the body known as **phospham**, PHN_2 (in a certain sense this is the analogue of N_3H polymerised, Chap. VI.). Indeed, phospham has been obtained by heating the products of the action of ammonia on phosphoric chloride, as an insoluble and alkaline powder, which gives ammonia and phosphoric acid when subjected to the action of water. The same substance is obtained by the action of ammonium chloride on phosphoric chloride (PNCl_2 is first formed, and reacts further with ammonia, forming phospham), and by igniting the mass which is formed by the action of ammonia on phosphorus trichloride. Formerly the composition of phospham was supposed to be PN_2 , but now there is reason to think that its molecular formula is $\text{P}_3\text{H}_3\text{N}_6$.

The above compounds correspond with normal salts, but nitriles and amides corresponding to acid salts are also possible, and they will be acids. For example, the amide $\text{PO}(\text{HO})_2(\text{NH}_2)$, and its nitrile, will be either $\text{PN}(\text{HO})_2$ or $\text{PO}(\text{HO})\text{NH}$, but at all events of the composition PNH_2O_2 , and having acid properties. The ammonium salt of this **phosphonitrilic acid** (it is called phosphamic acid), $\text{PNH}(\text{NH}_4)\text{O}_2$, is obtained by the action of ammonia on phosphoric anhydride, $\text{P}_2\text{O}_5 + 4\text{NH}_3 = \text{H}_2\text{O} + 2\text{PNH}(\text{NH}_4)\text{O}_2$. A non-crystalline soluble mass is thus formed, which is dissolved in a dilute solution of ammonia and precipitated with barium chloride, and the resultant barium salt is then decomposed with sulphuric acid, and thus a solution of the acid of the above composition is obtained.

It is evident from the theory of the formation of amides and nitriles (Chap. IX.) that very many compounds of this kind can correspond with the acids of phosphorus; but as yet only a few are known. The easy transitions of the ortho-, meta-, and pyro-phosphoric acids, by means of the hydrogen of ammonia, into the lower acids, and conversely, tend to complicate the study of this very large class of compounds, and it is rarely that the nature of a product thus obtained can be judged from its composition; and this is all the more so since instances of isomerism and polymerism, &c., are here possible. Many data are yet needed to enable us to form a true judgment as to the composition and structure of such compounds, although this subject was much studied by Liebig, Gerhardt, Gladstone, and others in former days, and more recently Thorpe, Mente, Stokes, and others have supplemented and corrected the former data. As an instance of the difficulties encountered we will describe the very interesting and most fully investigated compound of this class, PNCl_2 , called **chlorophosphamide**, or nitrogen chlorophosphorite. It is formed in small quantities when the vapour of phosphoric chloride is passed over ignited sal-ammoniac. Besson (1892) heated the compound $\text{PCl}_5, 8\text{NH}_3$ (which is easily and directly formed from PCl_5 and NH_3) under a pressure of about 50 mm. (of mercury) to 200° , and obtained brilliant crystals of PNCl_2 , which melted at 106° (in the residue after the distillation of sal-ammoniacal phospham). The chlorine in it is very stable—quite different from that in phosphoric chloride. Indeed, the resultant substance is not only insoluble in water (though soluble in alcohol and ether), but it is not even moistened by it, and distils over, together with steam, without being decomposed. In a free state it readily crystallises in colourless prisms, fuses at 114° , boils at 250° , and when fused with potash gives potassium

whose compounds, AsX_3 and AsX_5 , at once recall the metals. The hydrate of its highest oxide, arsenic acid (ortho-arsenic acid), H_3AsO_4 , is an oxidising agent, like the acids of the metals and easily gives up a portion of its oxygen to many other substances; but, nevertheless, it is very like phosphoric acid. Mitscherlich established the conception of isomorphism by comparing the salts of these acids.³⁰

Arsenic occurs in nature, not only combined with metals, but also, although rarely, native and also in combination with sulphur in two minerals—one red, *realgar*, As_2S_2 , and the other yellow, *orpiment*, As_2S_3 (Chap. XX., note 29). Arsenic occurs, but more rarely, in the form of salts of arsenic acid—for instance, the so-called cobalt and nickel blooms, two minerals which are found accompanying other cobalt ores, are the arsenates of these metals. Arsenic is also found in certain clays (ochres) and has been discovered in small quantities in some mineral springs, but it is in general of rarer occurrence in nature than phosphorus. Arsenic is most frequently extracted from arsenical pyrites, FeSAs , which, when roasted without access of air, evolves the vapour of arsenic, ferrous sulphide being left behind. It is also obtained by heating arsenious anhydride with charcoal, in which case carbonic oxide is evolved. In general, the oxides and other compounds are very easily reduced. Solid arsenic is a steel-grey brittle metal, having a bright lustre and scaly structure. Its specific gravity is 5.7. It is opaque and infusible, but volatilises without fusion (in a sealed vessel it fuses at about 480°) as a colourless or slightly yellow vapour, which, on cooling, deposits rhombohedral crystals.^{30a} The vapour

chloride and the amidonitrile of phosphoric acid. Judging from its formula and the simplicity of its composition and reactions, it might be thought that the molecular weight of this substance would be expressed by the formula PCl_2N , that it corresponds with PON and with PCl_5 (like POCl_3), with the substitution of Cl_3 by N, just as in POCl_3 two atoms of chlorine are replaced by oxygen; but all these surmises are incorrect, because its vapour density (referred to hydrogen—Gladstone, Wichelhaus) is 182—that is, the molecular formula must be three times greater, $\text{P}_3\text{N}_3\text{Cl}_6$. The polymerisation (tripling) is here of exactly the same kind as with the nitriles, metaphosphoric acid, and many other compounds of phosphorus.

³⁰ It is necessary to remark that, although arsenic is so closely analogous to phosphorus (especially in the higher forms of combination, RX_3 and RX_5), at the same time it exhibits a certain resemblance and even isomorphism with the corresponding compounds of sulphur (especially the lower metallic compounds of the type MAS , which correspond with MS). Thus compounds containing metals, arsenic, and sulphur are very frequently met with in nature. Sometimes the relative amounts of arsenic and sulphur vary, so that an isomorphous substitution between the arsenides and sulphides must be recognised. Besides FeS_2 (ordinary pyrites), and FeAs_2 , iron forms an arsenical pyrites containing sulphur and arsenic, which from its composition, FeAsS or $\text{FeS}_2\text{FeAs}_2$, resembles the two preceding.

^{30a} According to Retgers (1893) the arsenic mirror (see further on) is an unstable variety of metallic arsenic, whilst the brown product which is formed together with it in Marsh's apparatus is a lower hydride, AsH . Schuller and McLeod (1894), however,

density of arsenic is 150 times greater than that of hydrogen—that is, its molecule, like that of phosphorus, contains 4 atoms, As_4 . The vapour density decreases at about $1,700^\circ$, and corresponds to As_2 (V. Meyer, 1839). When heated in the air, arsenic easily oxidises into white arsenious anhydride, As_2O_3 , but even at the ordinary temperature it loses its lustre (becomes dull), owing to the formation of a coating of a lower oxide. The latter appears to be as volatile as arsenious anhydride, and it is probable that it is owing to the presence of this compound that the vapours of arsenious compounds, when heated with charcoal (for example, in the reducing flame of a blowpipe), have the characteristic smell of garlic, because the vapour of arsenic itself apparently has not this odour.

Arsenic easily combines with bromine and chlorine,³¹ while nitric

consider it to be a peculiar **yellow variety of arsenic**. This latter view is now generally accepted, because yellow arsenic in a solid form *soon passes into the ordinary metallic and opaque variety under the influence of the sun's rays* (but as far as I know it has not yet been shown whether hydrogen is evolved or not in this change), and this, together with its solubility in bisulphide of carbon, CS_2 , forms the chief characteristic of this substance (Erdmann and Unruh, 1901). It is obtained by heating metallic arsenic to volatilisation in a current of dry CO_2 , and rapidly cooling the resultant vapour in a stream of refrigerated CO_2 , and leading the mixture of arsenic vapour and CO_2 into vessels containing CS_2 which are kept in the dark and at a low temperature. The solution in CS_2 thus obtained deposits yellow crystals on evaporation. According to Prof. Erdmann the rise in the boiling-point of the CS_2 indicates that the molecule of arsenic has the composition As_4 , just as in a state of vapour. This variety of arsenic evidently corresponds to ordinary yellow phosphorus, P_4 , but is more unstable.

³¹ Hydrochloric acid dissolves arsenious anhydride in considerable quantities, and this is probably owing to the formation of unstable compounds in which the arsenious anhydride plays the part of a base. A compound called **arsenious oxychloride**, having the composition AsOCl , is even known. It is formed when arsenious anhydride is added little by little to boiling arsenic trichloride, $\text{As}_2\text{O}_3 + \text{AsCl}_3 = 3\text{AsOCl}$. It is a transparent substance, which fumes in air, and combines with water to form a crystalline mass having the composition $\text{As}(\text{OH})_2\text{Cl}$. When heated it decomposes into arsenious chloride and a fresh oxychloride of a more complex composition, $\text{As}_6\text{O}_8\text{Cl}_2$. Arsenic trichloride, when treated with a small quantity of water, forms the crystalline compound, $\text{As}(\text{OH})_3\text{Cl}$, mentioned above. These compounds resemble the basic salts of bismuth and aluminium. The existence of these compounds shows that arsenic is of a more metallic or basic character than phosphorus. Nevertheless **arsenic trichloride**, AsCl_3 , resembles phosphorus trichloride in many respects. It is obtained by the direct action of chlorine on arsenic, or by distilling a mixture of common salt, sulphuric acid, and arsenious anhydride. Arsenious chloride is a colourless oily liquid, boiling at 134° , and having a sp. gr. of 2.20. It fumes in air like other chloranhydrides, but is much more slowly and imperfectly decomposed by water than phosphorus trichloride. A considerable quantity of water is required for its complete decomposition into hydrochloric acid and arsenious anhydride. It forms an excellent example of the transition from true metallic chlorides to true chloranhydrides of the acids. It hardly combines with chlorine, i.e., if AsCl_5 is formed it is very unstable. **Arsenic tribromide**, AsBr_3 , is formed as a crystalline substance, fusing at 31° (Walden, 1902), and boiling at 221° , by the direct action of metallic arsenic on a solution of bromine in carbon bisulphide, the latter being then evaporated. The specific gravity of arsenic tribromide is 3.36. Crystalline arsenic tri-iodide, AsI_3 , having a sp. gr. 4.39, may be obtained in a like manner; it may be dissolved in water,

acid and aqua regia oxidise it into the higher oxide, or rather its hydrate, arsenic acid.³² As far as is known, it does not decompose steam, and acts exceedingly slowly on those acids, like hydrochloric, which are not capable of oxidising. It is employed in certain alloys—for instance, 1 to $\frac{1}{2}$ per cent. of arsenic is added to lead for making bullets in order to render it more fusible.

Arseniuretted hydrogen, arsine, AsH_3 , resembles phosphoretted hydrogen in many respects. This colourless gas, which liquefies into a mobile liquid at about -50° , and solidifies at about -110° , has a disagreeable garlic-like odour, is only slightly soluble in water, and is exceedingly poisonous. Even in small quantity it causes great suffering, and if present to any considerable amount in air it even causes death. The other compounds of arsenic are also poisonous,

and on evaporation separates out from the solution in an anhydrous state—that is, it is not decomposed—and consequently behaves like metallic salts. **Arsenic trifluoride, AsF_3 ,** is obtained by heating fluor spar and arsenious anhydride with sulphuric acid. It is a fuming, colourless, and very poisonous liquid, which boils at 63° and has a sp. gr. of 2.73. It is decomposed by water. It is very remarkable that fluorine forms a pentafluoride of arsenic also, although this compound has not yet been obtained in a separate state, but only in combination with potassium fluoride. This compound, K_3AsF_6 , is formed as prismatic crystals when potassium arsenate, K_3AsO_4 , is dissolved in hydrofluoric acid.

³² **Arsenic acid, H_3AsO_4 ,** corresponding with orthophosphoric acid, is formed by oxidising arsenious anhydride with nitric acid, and evaporating the resultant solution until it attains a sp. gr. of 2.2; on cooling it separates in crystals having the above composition. This hydrate corresponds with the normal salts of arsenic acid: but on dissolving in water (without heating), and on cooling a strong solution, crystals containing a greater amount of water, namely, $(\text{AsH}_3\text{O}_4)_2 \cdot \text{H}_2\text{O}$, separate. This water is easily expelled at 100° . At 120° crystals having a composition analogous with that of pyrophosphoric acid, $\text{As}_2\text{H}_4\text{O}_7$, separate, but water, on dissolving this hydrate with the development of heat, forms a solution in no way differing from a solution of ordinary arsenic acid, so that it is not an independent pyroarsenic acid that is formed. Neither is there any true analogue of metaphosphoric acid, but an intermediate hydrate of the composition $2\text{As}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$ is easily formed (Auger). Arsenic acid forms three series of salts, which are analogous with the three series of orthophosphates. Thus the normal salt, K_3AsO_4 , is formed by fusing the other potassium arsenates with potassium carbonate; it is soluble in water and crystallises in needles which do not contain water. Di-potassium arsenate, K_2HAsO_4 , is formed in solution by mixing potassium carbonate and arsenic acid until carbonic anhydride ceases to be evolved; it does not crystallise, and has an alkaline reaction; hence it corresponds perfectly with the sodium phosphate. As was mentioned above, arsenic acid itself acts as an oxidising agent; for example, it is used in the manufacture of aniline dyes for oxidising the aniline, and is prepared in large quantities for this purpose. When sulphuretted hydrogen is passed through its solution, sulphuric acid and arsenious anhydride are obtained in solution. When boiled with hydrochloric acid it evolves chlorine, like selenic, chromic, manganic, and certain other higher metallic acids.

Arsenic anhydride, As_2O_5 , is produced from arsenic acid at 180° . It must be carefully heated, as it decomposes into oxygen and As_2O_3 . Arsenic anhydride is an amorphous substance of sp. gr. 4.3 and almost insoluble in water, but it attracts moisture from the air, deliquesces, and passes into the acid. Hot water produces this transformation with great ease.

with the exception of the insoluble sulphur compounds.^{32a} Arseniuretted hydrogen, AsH_3 , is obtained by the action of water on the alloy of arsenic and sodium, sodium hydroxide and arseniuretted hydrogen being formed. It is also formed by the action of sulphuric acid on the alloy of arsenic and zinc: $\text{Zn}_3\text{As}_2 + 3\text{H}_2\text{SO}_4 = 2\text{AsH}_3 + 3\text{ZnSO}_4$.³³ The oxygen compounds of arsenic are very easily reduced by the action of hydrogen at the moment of its evolution from acids, and the reduced arsenic then combines with the hydrogen; hence, if a certain amount of an oxygen compound of arsenic be put into an apparatus containing zinc and sulphuric acid (and thus serving for the evolution of hydrogen),

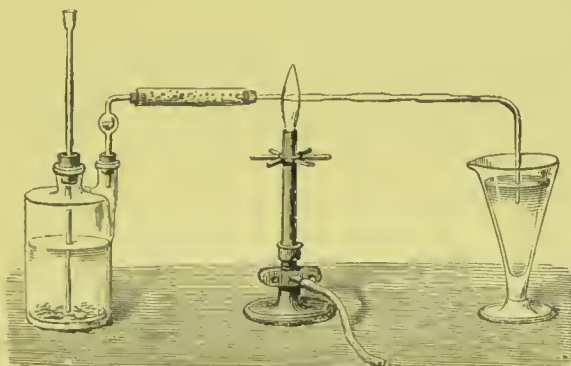


FIG. 95.—Formation and decomposition of arseniuretted hydrogen. Hydrogen is evolved in the Woulfe's bottle, and when the gas comes off, a solution containing arsenic is poured through the funnel. The presence of AsH_3 is recognised from the deposition of a mirror of arsenic when the gas-conducting tube is heated. If the escaping hydrogen be lighted, and a porcelain dish be held in the flame, a film of arsenic will be deposited on it. The gas is dried by passing through the tube containing calcium chloride. This apparatus is used for the detection of arsenic by Marsh's test.

the hydrogen evolved will contain arseniuretted hydrogen. In this case it is diluted with a considerable amount of hydrogen. But its presence in the most minute quantities may be easily recognised from the fact that it is **easily decomposed** by heat (at 200° according to Brunn) into metallic arsenic and hydrogen, and therefore, if such impure hydrogen be passed through a moderately heated tube, metallic arsenic will be deposited as a bright layer on the part of the tube which was heated (see note 30a). This reaction is so sensitive that it enables the most minute traces of arsenic to be discovered; hence it is employed in medical jurisprudence as a test in poisoning cases. It is easy to

^{32a} A. P. Borodin showed that arsenic acid (so long as it is not deoxidised) is far less poisonous than arsenious acid. A. Gauthier proposed (1902) and essayed the action of the methyl-sodium salt, $\text{As}(\text{CH}_3)\text{HNaO}_4$, known as 'arenal,' as a drug for decreasing fever, as the least poisonous of the soluble preparations of arsenic, many of which are employed in small quantities in medicine.

³³ The formation of arseniuretted hydrogen is accompanied by the absorption of 37,000 heat units, while phosphine evolves 18,000 (Ogier), and ammonia 27,000. Sodium (0.6 per cent.) amalgam, with a strong solution of As_2O_3 , gives a gas containing 86 vols. of arsenic and 14 vols. of hydrogen (Cavazzi).

discover the presence of arsenic in common zinc, copper, sulphuric and hydrochloric acids, &c., by this method. It is obvious that in testing for poison by Marsh's apparatus it is necessary to take zinc and sulphuric acid quite free from arsenic. The arsenic deposited in the tube may be driven as a volatile metal from one place to another in the current of hydrogen evolved, owing to its volatility. This forms a distinction between arseniuretted and antimoniuiretted hydrogen, which is decomposed by heat in just the same way as arseniuretted hydrogen, but the mirror given by Sb is not so volatile as that formed by As.

If hydrogen contains arseniuretted hydrogen, it also gives metallic arsenic when it burns, because in the reducing flame of hydrogen the oxygen attracted combines entirely with the hydrogen and not with the arsenic, so that if a cold object, such as a piece of china, be held in the hydrogen flame the arsenic will be deposited upon it as a metallic spot.³⁴

The most common compound of arsenic is the solid and volatile **arsenious anhydride**, As_2O_3 , which corresponds with phosphorous and nitrous anhydrides. This very poisonous, colourless, and sweet-tasting substance is generally known under the name of arsenic, or **white arsenic**. The corresponding hydrate is as yet unknown; its solutions, when evaporated, yield crystals of arsenious anhydride. It is chiefly prepared for the dyer, and is also used as a vermin-killer, and sometimes in medicine; it is a product from which all other compounds of arsenic can be prepared. It is obtained as a by-product in roasting cobalt

³⁴ This spot, or the metallic ring which is deposited on the heated tube, may easily be tested as to whether it is really due to arsenic or proceeds from some other substance reduced in the hydrogen flame—for instance, carbon or antimony. The necessity for distinguishing arsenic from antimony is all the more frequently encountered in medical jurisprudence, from the fact that preparations of antimony are very frequently used as medicine, and antimony behaves in the hydrogen apparatus just like arsenic, and therefore in making an investigation for poisoning by arsenic it is easy to mistake it for antimony. The best method to distinguish between the metallic spots of arsenic and antimony is to test them with a solution of sodium hypochlorite, free from chlorine, because this will dissolve arsenic and not antimony. Such a solution is easily obtained by the double decomposition of solutions of sodium carbonate and bleaching powder. A solution of potassium chlorate acts in the same manner, only more slowly. Further particulars must be looked for in analytical works.

Arseniuretted hydrogen, like phosphoretted hydrogen, is only slightly soluble in water, has no alkaline properties—that is, it does not combine with acids—and acts as a reducing agent. When passed into a solution of silver nitrate it gives a blackish-brown precipitate of metallic silver, the arsenic being oxidised. If acting on copper sulphate and similar salts, arseniuretted hydrogen sometimes forms arsenides—i.e., it reduces the metallic salt with its hydrogen, and is itself reduced to arsenic. Sulphuric, and even hydrochloric, acid reduces arseniuretted hydrogen to arsenic, and it is still more easily decomposed by arsenious chloride, and with phosphorous chloride it gives the compound PAs. Arseniuretted hydrogen gives metallic arsenic with an acid solution of arsenious anhydride (Tivoli).

and other ores containing arsenic. Arsenical pyrites are sometimes purposely roasted for the extraction of arsenious anhydride. When arsenical ores are burnt in the air, the sulphur and arsenic are converted into the oxides As_2O_3 and SO_2 . The former is a solid at the ordinary temperature, and the latter gaseous, and therefore the arsenious anhydride is deposited as a sublimate in the cooler portion of the flues through which the vapours escape from the furnace. It collects in condensing chambers specially constructed in the flues. The deposit is collected, and after being distilled gives arsenious anhydride in the form of a vitreous non-crystalline mass. This is one of the varieties of arsenious anhydride, which is also known in two crystalline forms. When sublimed—i.e., when it passes rapidly from the state of vapour to the solid state—it appears in the regular system in the form of octahedra.³⁵ It is obtained in the same form when it is crystallised from acid solutions. The specific gravity of the crystals is 3·7. The other crystalline form (in prisms) belongs to the rhombohedral system, and is also formed by sublimation when the crystals are deposited on a heated surface, or when it is crystallised from alkaline solutions.³⁶

Solutions of arsenious anhydride have a sweet metallic taste, and give a **feeble acid reaction**. Its solubility increases with the admixture of acids and alkalies. This as it were shows the property of arsenious anhydride of forming salts with acids and alkalies. And in fact compounds of it with hydrochloric acid (note 31), sulphuric anhydride

³⁵ According to Mitscherlich's determination, the vapour density of arsenious anhydride is 199 ($H=1$), that is, it answers to the molecular formula As_4O_6 . Probably this is connected with the fact that the molecule of free arsenic contains As_4 .

³⁶ Arsenious anhydride is obtained in an amorphous form after prolonged heating at a temperature near to that at which it volatilises, or, better still, by heating it in a closed vessel. It then fuses to a colourless liquid, which on cooling forms a transparent vitreous mass, whose specific gravity is only slightly less than that of the crystalline anhydride. On cooling, this vitreous mass undergoes an internal change, in which it crystallises and becomes opaque, and acquires the appearance of porcelain. The following difference between the vitreous and opaque varieties is very remarkable: when the vitreous variety is dissolved in strong and hot hydrochloric acid it gives crystals of the anhydride on cooling, and this crystallisation *is accompanied by the emission of light* (which is visible in the dark), and the entire liquid glows as the crystals begin to separate. The opaque variety does not emit light when the crystals separate from its hydrochloric acid solution. It is also remarkable that the vitreous variety passes into the opaque form when it is pounded—that is, under the action of a series of blows. Thus, several varieties of arsenious anhydride are known, but as yet they are not characterised by any special chemical distinctions, and even differ but little in their specific gravities, so that it cannot be said that the above differences are due to any isomeric transformation—that is, to an arrangement of the atoms in the molecule—but probably only depend on a difference in the distribution of the molecules, or, in other terms, are physical and not chemical variations. One part of the vitreous anhydride requires twelve parts of boiling water for its solution, or twenty-five parts at the ordinary temperature. The opaque variety is less soluble, and at the ordinary temperature requires about seventy parts of water for its solution.

(see further on), and with the alkali oxides are known.³⁷ If silver nitrate is added to a solution of arsenious anhydride, it does not give any precipitate unless a certain amount of the arsenious anhydride is saturated with an alkali—for instance, ammonia. It then gives a precipitate of silver arsenite, Ag_3AsO_3 . This is yellow, soluble in an excess of ammonia, and anhydrous; it shows distinctly that arsenious acid is tribasic, and that it differs in this respect from phosphorous acid, in which only two atoms of hydrogen can be replaced by metals.³⁸ The feeble acid character of arsenious anhydride is confirmed by the formation of saline compounds with acids. In this respect the most remarkable example is the anhydrous compound with sulphuric acid, having the composition $\text{As}_2\text{O}_3, \text{SO}_3$. It is formed in the roasting of arsenical pyrites in those spaces where the arsenious anhydride condenses, a portion of the sulphurous anhydride being converted into sulphuric anhydride, SO_3 , at the expense of the oxygen of the air. The compound in question forms colourless tabular crystals, which are

³⁷ Arsenious anhydride does not oxidise in air, either in a dry state or in solution, but in the presence of alkalis it absorbs oxygen from the air, and acts as a redneing agent. This probably is connected with the fact that arsenic acid is much more energetic than arsenious acid, and that it is arsenic acid which is formed by the oxidation of the latter in the presence of alkalis. Arsenious anhydride is easily reduced to arsenic by many metals, even by copper, and still more easily when ignited with carbon.

³⁸ The feebleness of the acid properties of arsenious anhydride is seen in the fact that if it be dissolved in ammonia water, and then a still stronger solution of ammonia be added, prismatic crystals separate having the composition of ammonium metarsenite, NH_4AsO_3 . This ammonium salt deliquesces in air, and loses all its ammonia. The magnesium salt is tri-metallic, $\text{Mg}_3(\text{AsO}_3)_2$; it is insoluble in water, and is formed by mixing an ammoniacal solution of arsenious anhydride with an ammoniacal solution of a magnesium salt. It is insoluble even in ammonia, although it dissolves in an excess of an acid. Magnesium hydroxide gives the same salt with arsenious solutions, and hence magnesia is one of the best antidotes for arsenic poisoning. The arsenites of copper are much used in the manufacture of colours, more especially of pigments. They are distinguished by their insolubility in water and by their remarkably vivid green colour, but at the same time by their poisonous character. Not only do such pigments applied to wall papers or other materials easily dust off from them, but they give exhalations containing AsH_3 . The cupric salts, CuX_2 , when mixed with an alkaline solution of arsenious acid, give a green precipitate of a copper salt called *Scheele's green*. Its composition is probably CuHAsO_3 . Ammonia dissolves it, and gives a colourless solution, containing cuprous arsenate—that is, the cupric compound is reduced and the arsenic subjected to oxidation. The so-called *Schweinfurt's green* was still more used, especially in former times; it is an insoluble green cupric salt, which resembles the preceding in many respects, but has a different tint. It is prepared by mixing boiling solutions of arsenious acid and cupric acetate. Arsenious acid forms with ferric hydroxide, FeAsO_4 , an insoluble compound; and this is the reason why freshly precipitated oxide of iron is employed as an *antidote for arsenic*. The freshly precipitated oxide of iron, taken immediately after poisoning by arsenic, converts the arsenious acid into an insoluble state, by forming a compound on which the acids of the stomach have no action, so that the poisoning cannot proceed. It is remarkable that the inhabitants of certain mountainous countries accustom themselves to taking arsenic, which, according to their experience, helps to overcome the fatigue of mountain ascents.

decomposed by water with formation of sulphuric acid and arsenious anhydride.³⁹

Antimony (stibium), $Sb = 120$, is another analogue of phosphorus. In its external appearance and the properties of its compounds it resembles the metals still more closely than arsenic does. In fact, antimony has the appearance, lustre, and many of the characteristic properties of the metals. Its oxide, Sb_2O_3 , exhibits the earthy appearance of rust or of lime, and has distinctly basic properties, although it corresponds with nitrous and phosphorous anhydride, and is able, like them, to give saline compounds with bases. At the same time antimony presents, in the majority of its compounds, a complete analogy with phosphorus and arsenic. Its compounds belong to the types SbX_3 and SbX_5 . It is found in nature chiefly in the form of sulphide, Sb_2S_3 . This substance sometimes occurs in large masses in mineral veins and is known in mineralogy under the name of antimony glance or **stibnite**, and commercially as **antimony** (Chap. XX., note 29). The most abundant deposits of antimony ore occur in Portugal (near Oporto on the Douro). Besides which antimony partially or totally replaces arsenic in some minerals; thus, for example, a compound of antimony sulphide and arsenic sulphide with silver sulphide is found in red silver ore. But in any case antimony is a rather rare metal found in few localities. In Russia it is known to occur in Daghestan in the Caucasus. It is extracted chiefly for the preparation of alloys with lead and tin, which are used for casting printing type.⁴⁰ Some of its compounds are also used in medicine, the most important in this respect being antimony pentasulphide, Sb_2S_5 (*sulfur auratum antimonii*), and tartar emetic, which is a double salt derived from tartaric acid and has the composition $C_4H_4K(SbO)O_6$. Even the native antimony sulphide is used in large quantities as a purgative for horses and dogs. Metallic antimony is extracted from the glance, Sb_2S_3 , by roasting, when the sulphur burns away and the antimony oxidises, forming the oxide Sb_2O_3 , which is then heated with charcoal, and thus reduced to a

³⁹ Adie (1889) obtained compounds of As_2O_3 with 1, 2, 4, and 8 SO_3 by the direct action of ordinary and Nordhausen sulphuric acid upon As_2O_3 . Weber had previously obtained $As_2O_3 \cdot SO_3$ (which disengages SO_3 at 225°), and also $As_2O_3 \cdot nSO_3$ (where $n = 5, 6$, and 8), by the action of the vapours of SO_3 upon As_2O_3 . The compound $As_2O_3 \cdot 8SO_3$ loses SO_3 at 100° . Oxide of antimony, Sb_2O_3 , gives similar compounds. Adie (1891) also obtained (by the action of SO_3 upon H_3PO_4) a compound $H_3PO_4 \cdot 3SO_3$ in the form of a viscous liquid decomposed by water.

⁴⁰ Printer's type consists of an alloy known as 'type-metal,' containing usually about 15 parts of antimony to 85 parts of lead; sometimes (for example, for stereotypes) from 10 to 15 per cent. of Bi or 8 per cent. of Sn and even Cu is added. The hardness of the alloy, which is essential for printing, evidently depends upon the presence of antimony; but an excess must be avoided, since this renders the alloy brittle, and the type after a time loses its sharpness.

metallic state. The reduction may be carried on in the laboratory on a small scale by fusing the sulphide with iron, which takes up the sulphur.^{40a}

Metallic antimony has a white colour and a brilliant lustre; it remains untarnished in the air, for the metal does not oxidise at the ordinary temperature. It crystallises in rhombohedra, and always shows a distinctly crystalline structure which gives it quite a different aspect from the majority of the metals yet known. Antimony is brittle, so that it is easily powdered; its specific gravity is 6.7, it melts at about 629.5° , but only volatilises at a bright-red heat. When heated in the air—for instance, before the blowpipe—it burns and gives white odourless fumes, consisting of the oxide. This oxide is termed **antimonious oxide**, although it might as well be termed antimonious anhydride. It is given the first name because in the majority of cases its compounds with acids are used, but it forms compounds with the alkalis just as easily.

Antimonious oxide, like arsenious anhydride, crystallises either in regular octahedra or in rhombic prisms; its specific gravity is 5.56; when heated it becomes yellow and then fuses, and when further heated in air it oxidises, forming an oxide of the composition Sb_2O_4 . Antimonious oxide is insoluble in water and in nitric acid, but it easily dissolves in strong hydrochloric acid and in alkalis, as well as in tartaric acid or solutions of its acid salts. When dissolved in the latter it forms tartar emetic. It is precipitated from its solutions in alkalis and acids (by the action of acids on the former and alkalis on the latter). It occurs native but rarely. As a base it gives salts of the type SbOX (as if the basic salts $= \text{SbX}_3, \text{Sb}_2\text{O}_3$) and hardly ever forms salts, SbX_3 . In the antimonyl salts, SbOX , the group SbO is univalent, like potassium or silver. The oxide itself is $(\text{SbO})_2\text{O}$, the hydroxide $\text{SbO}(\text{OH})$, &c.; tartar emetic is a salt in which one hydrogen of tartaric acid, $\text{C}_2\text{H}_4(\text{CO}_2\text{H})_2$ is replaced by potassium and the other by antimonyl, SbO . Antimonious oxide is very easily separated from its salts by any base, but it must be observed that this separation does not take place in the presence of tartaric acid, owing to the pro-

^{40a} Antimony is prepared in a state of greater purity by heating with charcoal the oxide obtained by the action of nitric acid on the impure commercial metallic antimony. This is based on the fact that by the action of the acid, antimony forms the oxide Sb_2O_3 , which is but slightly soluble in water. The arsenic, which is nearly always present, forms soluble arsenious and arsenic acids, and remains in solution. The purest antimony is easily obtained from tartar emetic, by heating it with a small quantity of nitre. Metallic antimony also occurs, although rarely, native; and as it is very easily obtained, it was known to the alchemists of the fifteenth century. Very pure metallic antimony may be deposited by the electric current from a solution of antimonious sulphide in sodium sulphide after the addition of sodium chloride to the solution.

perty of tartaric acid of forming a soluble double salt—i.e., tartar emetic.⁴¹

If metallic antimony, or antimonious oxide, is oxidised by an excess of nitric acid and the resultant mass carefully evaporated to dryness, **metantimonic acid**, SbHO_3 , is formed. Its corresponding potassium salt, $2\text{SbKO}_3 \cdot 5\text{H}_2\text{O}$, is prepared by fusing metallic antimony with one-fourth its weight of nitre and washing the resultant mass with cold water. This potassium salt is only slightly soluble in water (in 50 parts) and the sodium salt still less so. An ortho-acid, SbH_3O_4 , also appears to exist; ^{41a} it is obtained by the action of water on antimony pentachloride, but it is very unstable, like the pentachloride, SbCl_5 , itself, which easily gives up Cl_2 , leaving antimony trichloride, SbCl_3 , and this is decomposed by water, forming an oxychloride— SbOCl , only slightly soluble in water. When antimonic acid is heated to an incipient red heat, it parts with water and forms the anhydride, Sb_2O_5 , of a yellow colour and specific gravity 6.5.⁴²

⁴¹ As antimonious oxide answers to the type SbX_3 , it is evident that compounds may exist in which antimony will replace three atoms of hydrogen; such compounds have been to some extent obtained, but they are easily converted by water into substances corresponding with the ordinary formulæ of the compounds of antimony. Thus tartar emetic, $\text{C}_4\text{H}_4(\text{SbO})\text{K}_2\text{O}_6$, loses water when heated, and forms $\text{C}_4\text{H}_2\text{Sb}_2\text{K}_2\text{O}_6$ —that is, tartaric acid, $\text{C}_4\text{H}_6\text{O}_6$, in which one atom of hydrogen is replaced by potassium and three by antimony. But this substance is reconverted into tartar emetic by the action of water. A similar compound is seen in that **intermediate oxide of antimony** which is formed when antimonious oxide is heated in air; its composition is SbO_2 or Sb_2O_4 . This oxide may be regarded as ortho-antimonic acid, $\text{SbO}(\text{HO})_3$, in which three atoms of hydrogen are replaced by antimony—i.e., $\text{SbO}(\text{SbO}_3) = \text{Sb}_2\text{O}_4$. Oxide of antimony is also formed when antimonic acid is ignited; it then loses water and oxygen, and gives this intermediate oxide as a white infusible powder, of sp. gr. 6.7. It is somewhat soluble in water, and gives a solution which turns litmus paper red.

^{41a} Beilstein and Blaese (1889), after preparing many salts of antimonic acid, came to the conclusion that it is monobasic, but all the salts still contain water, so that their general type is mostly $\text{MSbO}_3 \cdot 3\text{H}_2\text{O}$, M being, for example, Li, Hg (salts of the suboxide), $\frac{1}{2}\text{Pb}$, &c. The type of the ortho-salts, M_3SbO_4 , is quite unknown, although it is reproduced in the thio-compounds, for instance, Schlippe's salt, Na_3SbS_4 ; but this salt also contains water of crystallisation, $9\text{H}_2\text{O}$ (Chap. XX., note 29).

⁴² Among the other compounds of antimony, **antimoniuretted hydrogen**, SbH_3 (by the action of acids upon the alloy Sb_2Mg_3) resembles arseniuretted hydrogen in its mode of formation and properties (it splits up at 150° , Brunn, 1890; when liquefied, it boils at -17° and solidifies at -28°), whilst the halogen compounds differ in many respects from those of arsenic. When chlorine is passed over an excess of antimony powder, it forms **antimony trichloride**, SbCl_3 , but if the chlorine be in excess it forms the pentachloride, SbCl_5 . The trichloride is a crystalline substance which melts at 72° and distills at 230° , whilst the pentachloride is a yellow liquid, which splits up into chlorine and the trichloride when heated; at 140° it begins to give off chlorine abundantly, and this carries away the vapour of the trichloride with it; at 200° the decomposition is complete, and pure antimonious chloride alone passes over. This property of antimony pentachloride has caused it to be applied in many cases for the transference of chlorine; all the more so, because when it has given up its chlorine, it leaves the trichloride, which is able to absorb a fresh amount of chlorine; and therefore many substances which are

The heaviest analogue of nitrogen and phosphorus is **bismuth**, $\text{Bi}=208$. Here, as in the other groups, the basic, metallic properties increase with the atomic weight. Bismuth does not give any hydrogen compound, and the highest oxide, Bi_2O_5 , is a very feeble acid oxide. Bismuthous oxide, Bi_2O_3 , is a base, and bismuth itself a perfect metal. To explain the other properties of bismuth it must further be remarked that it follows mercury, thallium, and lead, whose atomic weights are near to that of bismuth, and that therefore it resembles them and more especially its nearest neighbour, lead. Although PbO and PbO_2 represent types different from Bi_2O_3 and Bi_2O_5 , they resemble them in many respects, even in their external appearance, and moreover the lower oxides both of Pb and Bi are basic and the higher ones, which easily evolve oxygen, acid. But judging even by the formula, Bi_2O_3 is a more feeble base than PbO . They both easily give basic salts.

Bismuth, like P, As, and Pb, forms compounds of two types, BiX_3

unable to react directly with gaseous chlorine do so with antimony pentachloride, and in the presence of a small quantity of it chlorine will act on them, just as oxygen is able, in the presence of nitrogen oxides, to oxidise substances which could not be oxidised by means of free oxygen. Thus carbon bisulphide is not acted on by chlorine at low temperatures—this reaction requires a high temperature—but in the presence of antimony pentachloride its conversion into carbon tetrachloride takes place at low temperatures. Antimony tri- and penta-chlorides, having the character of chloranhydrides, fume in air, attract moisture, and are decomposed by water, forming antimonious and antimonic acids. But in the first action of water the trichloride does not evolve all its chlorine as hydrochloric acid, which is intelligible in view of the fact that antimonious anhydride is also a base, and is therefore able to react with acids; indeed antimony sulphide dissolved in an excess of hydrochloric acid (hydrogen sulphide is evolved) gives an aqueous solution of antimony trichloride, which, when carefully distilled, even gives the anhydrous compound. Antimony trichloride is only decomposed by an excess of water, and then not completely, for with a large quantity of water it forms *powder of algaroth*—i.e., antimony oxychloride. The first action of water consists in the formation of **oxychloride**, SbOCl , but the composition of the product varies with the relative amount of water, between the limits SbOCl and $\text{Sb}_4\text{O}_5\text{Cl}_2$. The latter compound is, as it were, a basic salt of the former, because its composition is $2(\text{SbOCl})\text{Sb}_2\text{O}_3$.

With bromine and iodine, antimony forms compounds similar to those with chlorine. Antimonious bromide, SbBr_3 , crystallises in colourless prisms, melts at 94° , and boils at 270° ; antimonious iodide, SbI_3 , forms red crystals of sp. gr. 5.0; antimony trifluoride, SbF_3 , separates from a solution of antimonious oxide in hydrofluoric acid, and SbF_3 is formed by a similar treatment of antimonic acid. The latter gives easily soluble double salts with the fluorides of the metals of the alkalis.

De Haën (1887) obtained very stable double soluble salts, SbF_3, KCl (100 parts of water dissolve 57 parts of salt), $\text{SbF}_3, \text{K}_2\text{SO}_4$, &c., which he proposed to make use of in the arts as very easily crystallisable and soluble salts of antimony. Engel, by passing hydrochloric acid gas into a saturated solution of antimonious chloride at 0° , obtained a compound $\text{HCl}, 2\text{SbCl}_3, 2\text{H}_2\text{O}$, and with the pentachloride a compound $\text{SbCl}_5, 5\text{HCl}, 10\text{H}_2\text{O}$. Bismuth trichloride, BiCl_3 , gives a similar compound. Ditte and Metzner (1892) showed that Sb and Bi dissolve in hydrochloric acid only owing to the participation of the oxygen of the air or of that dissolved in the acid.

and BiX_5 ,⁴³ which completely recall the two types we have already established for the compounds of lead. Just as in the case of lead, the type PbX_2 is basic, stable, easily formed, and passes with difficulty into the higher and lower types, which are unstable, so also in the case of bismuth the type of combination BiX_3 is the usual basic form. The higher type of combination, BiX_5 ,⁴⁴ behaves in fact toward this stable type, BiX_3 , in exactly the same manner as lead dioxide does to the monoxide; and bismuthic acid is obtained by the action of chlorine on bismuth oxide suspended in water, in exactly the same way as lead dioxide is obtained from lead oxide. It is an oxidising agent like lead dioxide, and even the acid character in bismuthic acid is only slightly more developed than in lead dioxide. Here, as in the case of lead (minium), intermediate compounds are easily formed in which the bismuth of the lower oxide plays the part of a base combined with the acid which is formed by the higher form of the oxidation of bismuth.

In nature, bismuth occurs in only a few localities and in small quantities, most frequently in a native state, and more rarely as oxide and as a compound of bismuth sulphide with the sulphides of other metals, and sometimes in gold ores. It is extracted from its native ores by simple fusion in the furnace shown in fig. 96. This furnace contains an inclined iron retort, into the upper extremity of which the ore is charged, and the molten metal flows from the lower extremity. It is

⁴³ Metallic bismuth is very easily obtained when the compounds of the oxide are reduced by powerful reducing agents, but when less powerful reducing agents—for example, stannous oxide—are taken, bismuth suboxide is formed as a black crystalline powder. It is a compound of the type BiX_2 , its composition being BiO ; it is decomposed by acids into the metal and oxide, which passes into solution.

⁴⁴ The type BiX_5 is represented by the pentoxide, Bi_2O_5 , its metahydrate, $\text{Bi}_2\text{O}_5 \cdot \text{H}_2\text{O}$, or BiHO_3 , known as bismuthic acid, and the pyrohydrate, $\text{Bi}_2\text{H}_4\text{O}_7$. **Bismuth pentoxide** is obtained by a prolonged passage of chlorine through a boiling solution of potassium hydroxide (sp. gr. 1.38), containing bismuth oxide in suspension; the precipitate is washed with water, with boiling nitric acid (but not for long, as otherwise the bismuthic acid is decomposed), then again with water, and finally the resultant bright red powder of the hydrate, BiHO_3 , is dried at 125° . The prolonged action of nitric acid on bismuthic anhydride, Bi_2O_5 , results in the formation of the compound $\text{Bi}_2\text{O}_4 \cdot \text{H}_2\text{O}$, which decomposes in moist air, forming Bi_2O_3 . The density of bismuthic anhydride is 5.10, that of the tetroxide, Bi_2O_4 , 5.60, and that of bismuthic acid, BiHO_3 , 5.75. **Pyrobismuthic acid**, $\text{Bi}_2\text{H}_4\text{O}_7$, forms a brown powder, which loses a portion of its water at 150° , and decomposes on further heating, with the evolution of oxygen and water. It is obtained by the action of potassium cyanide on a solution of bismuth nitrate. The meta-salts of bismuthic acid are known; for example, KBiO_4 . They generally occur, however, in combinations with meta-bismuthic acid itself. Thus, André (1891) took a solution of the double salt of BiBr_3 and KBr , treated it with bromine after adding ammonia, and obtained a red-brown precipitate, which after being washed (for several weeks) had the composition $\text{KBiO}_3 \cdot \text{HBiO}_3$. When washed with dilute nitric acid this salt gave bismuthic acid.

refined by re-melting, and the pure metal may be obtained by dissolving in nitric acid, decomposing the resultant salt with water, and reducing the precipitate by heating it with charcoal. Bismuth is a metal which

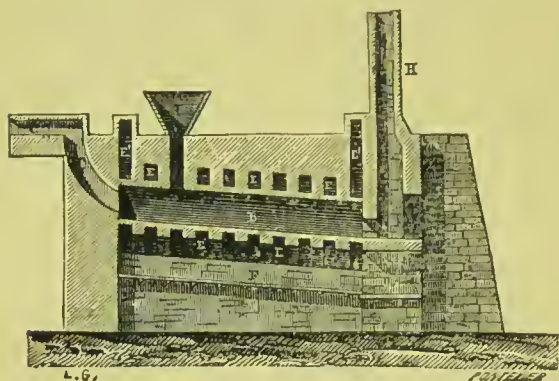


FIG. 96.—Furnace used for the extraction of bismuth from its ores.

crystallises very well from a molten state. Its specific gravity is 9.8; it melts at 269° , and if it is melted in a crucible, allowed to cool slowly, and the crust broken and the remaining molten liquid poured out, perfect rhombohedral crystals of bismuth are obtained on the sides of the crucible.^{41a}

It is brittle, has a grey-coloured fracture with a red-

dish lustre, is not hard, and is but very slightly ductile and malleable; it volatilises at a white heat and easily oxidises, but it does not become tarnished or oxidised at the ordinary temperature. It recalls antimony and lead in many of its properties. When oxidised in air, or when the nitrate is ignited, bismuth forms the **oxide**, Bi_2O_3 , as a white powder which fuses when heated and resembles massicot. The addition of an excess of caustic potash to a solution of a bismuthous salt gives a white precipitate of the hydroxide, $\text{Bi}(\text{OH})_3$, which loses its water and gives the anhydrous oxide when boiled with a solution of caustic potash. Both the hydroxide and oxide easily dissolve in acids and form bismuthous salts.

Bismuthous oxide, Bi_2O_3 , is a feeble and unenergetic base. The ortho-hydroxide, $\text{Bi}(\text{OH})_3$, parts with water and forms a metahydroxide (bismuthyl hydroxide), $\text{BiO}(\text{OH})$. Both of these hydroxides have their corresponding saline compounds of the compositions BiX_3 and BiOX . And the form BiOX is nothing else than the type of the basic salt, because $3\text{ROX} = \text{RX} + \text{R}_2\text{O}_3$. Many bismuth salts are formed according to the type BiOX , for instance, the carbonate, $(\text{BiO})_2\text{CO}_3$, which corresponds with the other carbonates M_2CO_3 . It is obtained as a white precipitate when a solution of sodium carbonate is added to a solution

^{41a} Hérard (1889) obtained a peculiar variety of bismuth by heating pure crystalline bismuth to a bright red heat in a stream of nitrogen. A greenish vapour was deposited in the cooler portions of the apparatus in the form of a grey powder, which, under the microscope, had the appearance of minute globules. An atmosphere of nitrogen is necessary for this transformation; other gases such as hydrogen and carbonic oxide do not favour the transition. The resultant amorphous bismuth fuses at 410° (the crystalline variety at 269°), and has the sp. gr. 9.483. (Does it not contain a nitride?)

of a bismuth salt.⁴⁵ The compound radicle BiO is not a special natural grouping, as it was formerly represented to be; it is simply a mode of expression for showing the relation between the compound in question and the compounds of other oxides.

Three **salts of nitric acid** are known containing bismuthous oxide. If metallic bismuth or its oxide is dissolved in nitric acid, it forms a colourless transparent solution containing a salt which separates in large transparent crystals containing $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$.^{45a} When heated at 72° these crystals melt, and at 75° already deposit an insoluble basic salt whose empirical formula is $\text{Bi}_2\text{N}_2\text{H}_2\text{O}_9$. If the preceding salt belongs to the type BiX_3 , this one should belong to the form BiOX , because it corresponds with $\text{BiO}(\text{NO}_3) + \text{Bi}(\text{HO})_2(\text{NO}_3)$. This salt may be heated to 150° without change. When the first colourless crystalline salt dissolves in water **it is decomposed**. There is no decomposition if an excess of acid is added to the water—that is to say, the salt is able to exist in an acid solution without decomposing, without separation of the so-called basic salt—but by itself it cannot be kept in solution; water decomposes this salt, acting on it like an alkali. In other words, the basic properties of bismuthic oxide are so feeble that even water acts by taking up a portion of the acid from it. Here we see one of the most striking facts, long since observed, confirming that action of water on salts about which we have spoken in Chapter X. and elsewhere. This action of water may be expressed thus:— $\text{BiX}_3 + 2\text{H}_2\text{O} = \text{Bi}(\text{OH})_2\text{X} + 2\text{XH}$. A salt of the type $\text{Bi}(\text{OH})_2\text{X}$ is obtained in the precipitate. But if the quantity of acid, HX , be increased, the salt BiX_3 will again be formed and will pass into solution. The quantity of the salt BiOX which passes into solution on the addition of a given quantity of acid depends indisputably on the amount (mass) of water (Muir). The solution, which is perfectly transparent with a small amount of water, becomes cloudy and deposits the salt of the type BiOX , when diluted. The white flaky precipitate of $\text{Bi}(\text{OH})_2\text{NO}_3$ formed from the normal salt, $\text{Bi}(\text{NO}_3)_3$, by mixing it with five parts of water, and

⁴⁵ Basic bismuth carbonate is employed for whitening the skin (veloutine).

^{45a} Rutten (1902) showed that oxide of bismuth, or the above-mentioned neutral salt, under the action of an excess of monohydrated nitric acid (at the ordinary temperature), forms a crystalline powder containing far less water: $\text{Bi}_2(\text{NO}_3)_{10} \cdot 3\text{H}_2\text{O}$. Rutten also observed that if sufficient water is added to strong HNO_3 to form an acid capable of dissolving the pentahydrated salt without decomposing it, and then strong nitric acid is added to the saturated solution, it forms a transparent, gelatinous, colloidal mass, which subsequently deposits the above less-hydrated crystals. The system composed of oxide of bismuth, nitric acid, and water presents a most instructive instance of chemical equilibrium in dependence upon the pressure, temperature, and the relative amounts of the component substances and their combination and state (phase).

in general with a small amount of water, is used in medicine under the name of *magisterium bismuthi*.⁴⁶

Metallic bismuth is used in the preparation of fusible alloys. The addition of bismuth to many metals renders them very hard, and at the same time generally lowers their melting-points to a considerable extent. Thus Wood's metal, which contains one part of cadmium, one of tin, two of lead, and four of bismuth, fuses at about 60° .⁴⁷ Rose's alloy, which fuses at 96° , contains two parts of Bi, one of Sn and one of Pb; and in general many alloys composed of bismuth, tin, lead, and antimony melt below or about the boiling-point of water.

Just as in group II., side by side with the elements zinc, cadmium, and mercury in the uneven series, we found calcium, strontium, and barium in the even series; and as in group IV., parallel to silicon, germanium, tin, and lead, we noticed thallium, zirconium, cerium, and thorium; so also in group V. we find, beside the elements of the uneven series P, As, Sb, and Bi, a series of analogues in the even series, which, with a certain degree of similarity (mainly quantitative, or relative to the atomic weights), also present a series of particular (qualitative) independent points of distinction. In the even series **vandium**, **niobium**, and **tantalum** are known. Just as bismuth is similar in many respects to its neighbour lead, so also do V, Nb, and Ta resemble their nearest neighbours in the other groups, Ti, Zr, Cr, Mo, and W, even in their external appearance, not to mention the nature of their com-

⁴⁶ With an excess of water a further quantity of acid is separated and a still more basic salt formed. The ultimate product, on which an excess of water has apparently no action whatever, is a substance having the composition $\text{BiO}(\text{NO}_3)\cdot\text{BiO}(\text{OH})$. If we refer all the bismuthous compounds to the type, Bi_2X_6 , we shall obtain the following expression for the composition of the nitrates: normal salt, $\text{Bi}_2(\text{NO}_3)_6$; first basic salt, $\text{Bi}_2\text{O}(\text{OH})_2(\text{NO}_3)_2$; *magisterium bismuthi*, $\text{Bi}_2(\text{OH})_4(\text{NO}_3)_2$, and the limiting form $\text{Bi}_2\text{O}_2(\text{OH})(\text{NO}_3)$.

The general character of bismuthous oxide in its compounds is well exemplified in the nitrate; **bismuthous chloride**, BiCl_3 , which is obtained by heating bismuth in chlorine, or by dissolving it in aqua regia, and then distilling without access of air, is also decomposed by water in exactly the same manner, and forms basic salts—for instance, first, BiOCl , &c. Bismuth chloride boils at 447° , and its formula is probably BiCl_3 . Polymerisation may take place in some compounds and not in others. A volatile compound of the composition $\text{Bi}(\text{C}_2\text{H}_5)_3$ is also known as a liquid which is insoluble in water and decomposes with explosion when heated at 130° . Double salts containing chloride of bismuth are: $2(\text{KCl})\cdot\text{BiCl}_3\cdot 2\text{H}_2\text{O}$ (from a solution of Bi_2O_3 and KCl in hydrochloric acid) and $\text{KCl}\cdot\text{BiCl}_3\cdot\text{H}_2\text{O}$. Bigham (1892) also obtained $\text{KBr}(\text{SO}_4)_2$ in tabular crystals by treating the above-named double salt with strong sulphuric acid. The composition of this salt recalls that of alumn.

⁴⁷ As this alloy is fusible, it may be employed in the place of mercury in many physical experiments conducted at or above 70° , and it offers the advantage that its vapour has no appreciable pressure (mercury at 100° , 0.75 mm). Bismuth expands in passing into a molten state, but it has a temperature of maximum density. According to Luedeking the mean coefficient of expansion of liquid bismuth is 0.0000442 (between 270° and 303°), and that of solid bismuth 0.0000411.

pounds, naturally taking into account the differences of type corresponding with the different groups. The occurrence in group V. determines the type of the oxides, R_2O_3 and R_2O_5 , and the development of an acid character in the higher oxides. The occurrence in the even series determines the absence of volatile compounds, RH_3 , for these metals, and a more basic character of the oxides of a given composition than in the uneven series, &c. Vanadium, niobium, and tantalum belong to the category of rare metals, and are exceedingly difficult to obtain pure, owing more especially to their similarity to, and occurrence with, chromium, tungsten, and other metals, and also in combination among themselves; it is, therefore, natural that they have been far from completely studied, although since 1860 chemists have devoted not a little time to their investigation. The researches carried out by Marignac, at Geneva, on niobium, and by Sir Henry Roscoe, at Manchester on vanadium deserve special attention.⁴⁸ The undoubted qualitative resemblance between the compounds of vanadium and those of chromium, as well as the want of completeness in the knowledge of the compounds of vanadium, long caused its oxides to be considered analogous in atomic composition to those formed by chromium. The higher oxide of vanadium was therefore supposed to have the formula VO_3 . But, as a matter of fact, the chemical analogy of the elements does not hold in one direction only; vanadium is at one and the same time the analogue of chromium, group VI., and also the analogue of phosphorus, arsenic, and antimony; just as bismuth is related to both lead and antimony. We should have to extend our description considerably if we wished to give the complete history, even of vanadium alone, not to mention niobium and tantalum, especially as some of the questions concerning the compounds of these elements have not yet been fully elucidated. We shall therefore limit ourselves to pointing out the most important features in the history of these elements, since the minerals themselves in which they occur are exceedingly rare and only accessible to a few investigators.

An important point in the history of the members of this group is the circumstance that they form volatile compounds with chlorine, similar to the compounds of the elements of the phosphorus group, namely, to those of the type RX_5 . The vapour densities of the compounds of these elements were determined, and served as the most important basis for the explanation of the molecular composition of

⁴⁸ Roscoe demonstrated the quantitative analogy of the vanadium and phosphorus compounds and the qualitative analogy of the vanadium and chromium compounds, which was an unexpected and important discovery at the time. The periodic law explained and generalised these relations.

these molecules. In this we see the power of general and fundamental laws, like that of Avogadro-Gerhardt. An oxychloride, VOCl_3 , is known for vanadium, which is the perfect analogue of phosphorus oxychloride. It was formerly considered to be vanadium chloride, for just as in the case of uranium (Chap. XXI.), its lower oxide, VO , was considered to be the metal, because it is exceedingly difficultly reduced—even potassium does not remove all the oxygen, besides which it has a metallic appearance, and decomposes acids like a metal; in a word, it simulates a metal in every respect. **Vanadium oxychloride** is obtained by heating the trioxide, V_2O_3 , mixed with charcoal, in a current of hydrogen; the lower oxide of vanadium is then formed, and this, when heated in a current of dry chlorine, gives the oxychloride VOCl_2 as a reddish liquid which does not act on sodium and may be purified by distillation over this metal. It fumes in the air, giving reddish vapours; it reacts on water, forming hydrochloric and vanadic acids; hence it is very similar, on the one hand, to phosphorus oxychloride, and, on the other hand, to chromium oxychloride, CrO_2Cl_2 (Chap. XXI.). It is of a yellow colour, its specific gravity is 1.83, it boils at 120° , and its vapour density is 86 with respect to hydrogen; therefore the above formula expresses its molecular weight.⁴⁹

Vanadic anhydride, V_2O_5 , is obtained either in small quantities from certain clays where it accompanies the oxides of iron (hence some sorts of iron contain vanadium) and phosphoric acid, or from the rare minerals: volborthite, CuHVO_4 , or basic vanadate of copper; vanadinite, $\text{PbCl}_2 \cdot 3\text{Pb}_3(\text{VO}_4)_2$; lead vanadate, $\text{Pb}_3(\text{VO}_4)_2$, &c.^{49a} The latter salts are carefully ignited for some time with one-third of their weight of nitre, the fused mass being powdered and boiled in water; the yellow solution obtained contains potassium vanadate. The solution is neutralised with acid, and barium chloride added; a meta-salt, $\text{Ba}(\text{VO}_3)_2$, is then precipitated as an almost insoluble white powder, which gives a solution of vanadic acid when boiled with sulphuric acid.

⁴⁹ When vanadium oxychloride is heated with zinc in a closed tube at 400° , it loses a portion of its chlorine and forms a green crystalline mass of sp. gr. 2.88, which is deliquescent in air and has the composition VOCl_2 . Only its vapour density is unknown, and it would be extremely important to determine whether its molecular composition is that given above, or whether it corresponds with the formula $\text{V}_2\text{O}_3\text{Cl}_4$. Another less volatile oxychloride, VOCl , is formed with it as a brown insoluble substance, which is, however, soluble in nitric acid like the preceding. Roscoe obtained a still lower chlorinated substance, namely, $(\text{VO})_2\text{Cl}$; but it may only consist of a mixture of VO and VOCl . At all events, we here find a graduated series such as is met with in the compounds of very few other elements.

^{49a} A mineral called Roscoelite rich in vanadium has been found in California. The fact that compounds of vanadium have been found in the mother liquors obtained in the manufacture of soda and beet-sugar shows that traces of this element are widely distributed in nature.

(The precipitate is at first yellow, as long as it remains amorphous, but it afterwards becomes crystalline and white.) The solution thus obtained is neutralised with ammonia, thus forming ammonium (meta-) vanadate, NH_4VO_3 , which, when evaporated, gives colourless crystals, insoluble in water, containing sal-ammoniac; this salt is hence precipitated by adding solid sal-ammoniac to the solution.^{49b} Ammonium vanadate, when ignited, leaves vanadic acid behind. In this it differs from the corresponding chromium salt, which is deoxidised into chromium oxide when ignited. In general, vanadic acid has but a slight oxidising action. It is reduced with difficulty, like phosphoric or sulphuric acid, and in this differs from arsenic and chromic acids. Vanadic acid, like chromic acid, separates from its solution as the anhydride V_2O_5 , and not in a hydrous state. Vanadic anhydride, V_2O_5 , forms a reddish-brown mass, which readily fuses and re-solidifies into transparent crystals having a violet lustre (another point of resemblance to chromic acid); it dissolves in water, forming a yellow solution with a slightly acid reaction.⁵⁰

^{49b} With peroxide of hydrogen, NH_4VO_4 is easily formed. It corresponds to the peroxide compound, pervanadic acid, HVO_4 , of the same type as persulphuric and perchromic acids (see following chapter.)

⁵⁰ Strong acids and alkalis dissolve vanadic anhydride in considerable quantities, forming yellow solutions. When it is ignited, especially in a current of hydrogen, it evolves oxygen and forms the lower oxides: V_2O_4 (acid solutions of a green colour, like the salts of chromic oxide), V_2O_3 , and the lowest oxide, VO . The latter is the metallic powder which is obtained when vanadium oxychloride is heated in an excess of hydrogen, and was formerly mistaken for metallic vanadium. When a solution of vanadic acid is treated with metallic zinc it forms a blue liquid, which seems to contain this oxide. It acts as a reducing agent (and forms a close analogue to chromous oxide, CrO). Metallic **vanadium** can only be obtained from vanadium chloride which is quite free from oxygen. Moissan (1893) obtained it by reducing the oxide with carbon in the electric furnace, and considered it to be the most infusible of the metals in the series Pt, Cr, Mo, U, W, and V (he also obtained a compound of vanadium and carbon). The specific gravity of this metal is 5.5. It is of a greyish-white colour, is not decomposed by water, and is not oxidised in air, but burns when strongly heated, and can be fused in a current of hydrogen (perhaps forming a compound with hydrogen). It is insoluble in hydrochloric acid, but easily dissolves in nitric acid, and when fused with caustic soda forms sodium vanadate.

As regards the salts of vanadic acid, three different classes are known: the first correspond with metavanadic acid, $\text{VMO} = \text{M}_2\text{OV}_2\text{O}_5$, the second correspond with the dichromates—that is, have the composition $\text{V}_4\text{M}_2\text{O}_{11}$, which is equal to $\text{M}_2\text{O} + 2\text{V}_2\text{O}_5$,—and the third with orthovanadic acid, VM_3O_4 or $3\text{M}_2\text{O} + \text{V}_2\text{O}_5$. The latter are formed when vanadic anhydride is fused with an excess of an alkaline carbonate.

Vanadic acid gives the so-called 'complex' acids (which are considered more fully in Chap. XXI. when speaking of Mo and W)—i.e., acids formed of two acids assimilated into one. Thus, Friedheim (1890) obtained phosphor-vanadic acid, and Schmitz-Dumont (1890) a similar arseno-vanadic acid. The former is obtained by heating V_2O_5 with syrupy phosphoric acid. The resultant golden-yellow tabular crystals have the composition $\text{H}_2\text{O}, \text{V}_2\text{O}_5, \text{P}_2\text{O}_5, 9\text{H}_2\text{O}$, and there are corresponding salts—for example, $(\text{NH}_4)_2\text{V}_2\text{O}_5, \text{P}_2\text{O}_5$ with 3 and $7\text{H}_2\text{O}$, &c. These salts cannot be separated by crystallisation, so that there are 'complexes' of these acids in a whole series of salts (and also in nature). It may be supposed (Friedheim) that V_2O_5 here plays, as it were, the part of a

Niobium and tantalum ⁵¹ occur as acids in rare minerals, and are mainly extracted from tantalite and columbite, which are found in Bavaria, Finland, North America, and in the Urals. These minerals are composed of the ferrous salts of niobic and tantalic acids; they contain about 15 per cent. of ferrous oxide in isomorphous mixture with manganous oxide, in combination with various proportions of tantalic and niobic anhydrides. These minerals are first fused with a considerable amount of potassium bisulphate, and the fused mass is boiled in water, which dissolves the ferrous and potassium salts and leaves an insoluble residue of impure niobic and tantalic acids. This raw product is then treated with ammonium sulphide, in order to extract the tin and tungsten, which pass into solution. The residue containing the acids (according to Marignac) is then treated with hydrofluoric acid, in which it entirely dissolves, and potassium fluoride is added to the resultant hot solution; on cooling, a sparingly soluble double fluoride of potassium and tantalum separates out in fine crystals, while the much more soluble niobium salt remains in solution. The difference in the solubility of these double salts in water acidified with hydrofluoric acid (in pure water the solution becomes cloudy after a

base, or that these acids may be looked upon as double salts. Of the true double salts of vanadium (Nb and Ta), very many are known among the fluorides, such as $\text{VF}_3 \cdot 2\text{NH}_4\text{F}$, $\text{VOF}_2 \cdot 2\text{NH}_4\text{F}$, $\text{VO}_2\text{F}_2 \cdot 3\text{NH}_4\text{F}$, &c. (Pettersson, Piccini, and Georgi, 1890-92). V_2O_3 also gives a double salt having the composition of an alum.

Vanadium was discovered at the beginning of this century by Del-Rio, and was afterwards investigated by Sefström, but it was only in 1868 that Roscoe established the above formulæ of the vanadic compounds.

⁵¹ The researches made by Roscoe were preceded by those of Marignac in 1865, on the **niobium and tantalum compounds**, to which were also ascribed formulæ different from those now recognised. Tantalum was discovered simultaneously with vanadium by Hatchett and Ekeberg, and was afterwards studied by Rose, who in 1844 discovered niobium in it. Notwithstanding the numerous researches of Hermann (in Moscow), Kobell, Rose, and Marignac, there is as yet no certainty as to the purity of, and the properties ascribed to, the compounds of these elements. They are difficult to separate from each other, and especially from the cerite metals and titanium, &c., which accompany them. Before the investigations of Rose the highest oxide of tantalum was supposed to belong to the type TaX_6 —that is, its composition was taken as TaO_3 , and to the lower oxide was ascribed a formula TaO_2 . Rose gave the formula TaO_2 to the higher oxide, and discovered a new element called niobium in the substance previously supposed to be the lower oxide. He even admitted the existence of a third element occurring together with tantalum and niobium, which he named pelopium, but he afterwards found that pelopie acid was only another oxide of niobium, and he considered it probable that the higher oxide of this element is NbO_3 , and the lower Nb_2O_3 . Hermann found that niobic acid which was considered pure contained a considerable quantity of tantalic acid, and besides this he admitted the existence of another special metallic acid, which he called ilmenic acid, after the locality (the Ilmen mountains of the Urals) of the mineral from which he obtained it. V. Kobell recognised still another acid, which he called dianic acid, and these diverse statements were only brought into agreement in the sixties by Marignac. He first of all indicated an accurate method for the separation of tantalic and niobic compounds, which are always obtained in admixture.

certain time) is so great that the tantalum compound requires 150 parts of water for its solution, and the niobium compound only 13 parts. The Greenland columbite (specific gravity 5·36) contains only niobic acid, and that from Bodenmais, Bavaria (specific gravity 6·06), almost equal quantities of tantalic and niobic acids. Having isolated tantalic and niobic salts, Marignac found that the relation between the potassium and fluorine in them is very variable—that is, that there exist various double salts of fluoride of potassium with the fluorides of the metals of this group, but that with an excess of hydrofluoric acid both the tantalum and niobium compounds contain seven atoms of fluorine to two of potassium, whence it must be concluded that the simplest formula for these double salts will be $K_2RF_7=RF_5, 2KF$; that is, that the type of the higher compounds of niobium and tantalum is RX_5 , and is hence similar to phosphoric acid. A chloride, $TaCl_5$, may be obtained from pure tantalic acid by heating it with charcoal in a current of chlorine. This is a yellow crystalline substance, which melts at 211° , and boils at 241° ; its vapour density with respect to hydrogen is 180, as would follow from the formula $TaCl_5$. It is completely decomposed by water into tantalic and hydrochloric acids. **Niobium pentachloride** may be prepared in the same manner; it fuses at 194° , and boils at 240° . When treated with water this substance gives a solution containing niobic acid, which only separates out on boiling the solution. Delafontaine and Deville found its vapour density to be 9·3 (air = 1), as is indicated by its formula $NbCl_5$.⁵² In general, vanadium, niobium and tantalum form, as far as we know,

⁵² If niobic acid is mixed with a small quantity of charcoal and ignited in a stream of chlorine, a difficultly fusible and difficultly volatile oxychloride, $NbOCl_3$, separates. The vapour density of this compound with respect to air is 7·5, and this vapour density completely confirms the accuracy of the formulæ given by Marignac, and indicates the quantitative analogy between the compounds of niobium and tantalum, and those of phosphorus and arsenic, and consequently also of vanadium. In their qualitative relations, as is evident also from the correspondence of the atomic weights, the compounds of tantalum and niobium exhibit a great analogy with those of molybdenum and tungsten. Thus, zinc, when acting on acid solutions of tantalic and niobic compounds, gives a blue coloration, exactly as it does with those of tungsten and molybdenum (also titanium). These acids form the same large number of salts as those of tungsten and molybdenum. The anhydrides of the acids are also insoluble in water, but are sometimes held in solution as colloids, just like those of titanic and molybdic acids. Furthermore, niobium is in every respect the nearest analogue of molybdenum, and tantalum of tungsten. **Niobium** is obtained by reducing the double fluoride of niobium and sodium with sodium. It is difficult to obtain in a pure state. It is a metal on which hydrochloric acid acts with some energy, as also does hydrofluoric acid mixed with nitric acid, and also a boiling solution of caustic potash. **Tantalum**, which is obtained in exactly the same way, is a much heavier metal. It is infusible, and is only acted on by a mixture of hydrofluoric and nitric acids. Rose, in 1868, showed that in the reduction of the double fluoride, $NbF_5, 2KF$, by sodium, a greyish powder is obtained after treating with water. The specific gravity of this powder is 6·3, and he considers it to be niobium

compounds corresponding to the types RX , RX_2 , RX_3 , RX_4 and RX_5 , and this multiplicity of forms, which recalls manganese and nitrogen, renders the investigation of these very rare elements somewhat difficult.

hydride, NbH . Neither did he obtain metallic niobium when he reduced with magnesium and aluminium, but an alloy, Al_3Nb , having a sp. gr. of 4.5.

Niobium, so far as is known, unites in three proportions with oxygen. NbO , which is formed when $NbOF_3 \cdot 2KF$ is reduced by sodium; NbO_2 , which is formed by igniting niobic acid in a stream of hydrogen, and niobic anhydride, Nb_2O_5 , a white infusible substance, which is insoluble in acids and has a specific gravity of 4.5. Tantalalic anhydride closely resembles niobic anhydride, and has a specific gravity of 7.2. The **tantalates** and **niobates** present the type of ortho-salts—for example, $Na_2HNbO_4 \cdot 6H_2O$, and also of pyro-salts, such as $K_3HNb_2O_7 \cdot 6H_2O$, and of meta-salts—for example, $KNbO_3 \cdot 2H_2O$. And, besides these, they give salts of a more complex type, containing a larger amount of the elements of the anhydride; thus, for instance, when niobic anhydride is fused with caustic potash it forms a salt which is soluble in water, and crystallises in monoclinic prisms, having the composition $K_3Nb_6O_{19} \cdot 16H_2O$. There is a perfectly similar isomorphous salt of tantalalic acid. Tantalite is a salt of the type of metatantalalic acid, $Fe(TaO_3)_2$. The composition of yttrotantalite appears to correspond with that of orthotantalalic acid.

CHAPTER XX

SULPHUR, SELENIUM, AND TELLURIUM

THE acid character of the higher oxides RO_3 of the elements of group VI. is still more clearly defined than that of the higher oxides of the preceding groups, whilst feeble basic properties only appear in the oxides RO_3 of the elements of the even series, and then only for those elements having a high atomic weight—that is, under those two conditions in which, as a rule, the basic characters increase. Even the lower types RO_2 and R_2O_3 , &c., formed by the elements of group VI., are acid anhydrides in the uneven series, and only those of the elements of the even series have the properties of peroxides or even of bases.

Sulphur is the typical representative of group VI., both on account of the fact that the acid properties of the group are clearly defined in it and also because it is more widely distributed in nature than any of the other elements belonging to this group. Sulphur gives the typical compounds, H_2S , sulphuretted hydrogen, SO_3 , sulphuric anhydride, and SO_2 , sulphurous anhydride. And in all of them we find acid properties— SO_3 and SO_2 are anhydrides of acids, and H_2S is an acid, although a feeble one. As an element, sulphur has all the properties of a true non-metal; it has not a metallic lustre, does not conduct electricity, is a bad conductor of heat, is transparent, and combines directly with metals—in short, it has all the properties of the non-metals, like oxygen and chlorine. Furthermore, sulphur exhibits a distinct quantitative **resemblance to oxygen**, especially in the fact that, like oxygen, it combines **with two atoms of hydrogen**, and forms compounds resembling oxides with metals and non-metals. From this point of view sulphur is bivalent, if the halogens are univalent.¹ The chemical character of

¹ The individuality of sulphur is most clearly defined in its organo-metallic compounds. Not to dwell on this vast subject, which belongs to the province of organic chemistry, I think it not superfluous to compare the physical properties of the ethyl compounds of mercury, zinc, sulphur, and oxygen. The composition of all of them is expressed by the general formula $(\text{C}_2\text{H}_5)_2\text{R}$, where $\text{R} = \text{Hg}, \text{Zn}, \text{S}, \text{or O}$. They are all volatile: mercury ethyl, $\text{Hg}(\text{C}_2\text{H}_5)_2$, boils at 159° , its sp. gr. is 2.444, and its molecular volume, 106; zinc ethyl boils at 118° , has the sp. gr. 1.882, and the volume 101; ethyl sulphide, $\text{S}(\text{C}_2\text{H}_5)_2$, boils at 90° , has the sp. gr. 0.825, and the volume 107; common ether,

sulphur is clearly expressed by the fact that it forms a very slightly stable and feebly energetic acid with hydrogen. The salts corresponding with this acid are the sulphides, just as the oxides correspond to water and the chlorides to hydrochloric acid. However, as we shall afterwards see more fully, the sulphides are more closely analogous to the former than to the latter. But although combining with metals, as oxygen does, sulphur also forms chemically stable compounds with oxygen, and this fact impresses a peculiar character on all the relations of this element.²

Sulphur belongs to the number of those elements which **are very widely distributed in nature**, and it occurs both free and combined in various forms. The atmosphere, however, is almost entirely free from compounds of sulphur, although a certain amount of them should be present, if only from the fact that sulphurous anhydride is emitted from the earth in volcanic eruptions, and occurs in the air of cities, where much coal is burnt, since this always contains FeS_2 . Sea and river water generally contain more or less sulphur in the form of sulphates. The beds of gypsum, sodium sulphate, magnesium sulphate, and the like are formations of undoubtedly aqueous origin. The sulphates contained in the soil are the source of the sulphur found in plants, and are indispensable to their growth. Among vegetable substances, the proteids always contain from one to two per cent. of sulphur. From plants the albuminous substances, together with their sulphur, pass into the animal organism, and the decomposition of animal matter is accompanied by the odour of sulphuretted hydrogen as the product into which the sulphur passes in the decomposition of the albuminous substances. Thus, a rotten egg emits sulphuretted hydrogen. Sulphur occurs largely in nature, as the various insoluble sulphides of the metals. Iron, copper, zinc, lead, antimony, arsenic, &c., occur in nature combined with sulphur. These **metallic sulphides** frequently have a metallic lustre, and in the majority of cases occur

or ethyl oxide, $\text{O}(\text{C}_2\text{H}_5)_2$, boils at 35° has the sp. gr. 0.736, and the volume 101, in addition to which diethyl itself, $(\text{C}_2\text{H}_5)_2 = \text{C}_4\text{H}_{10}$, boils at about 0° , has a sp. gr. about 0.62, and a volume of about 94. Thus, the substitution of Hg, S, and O scarcely changes the volume, notwithstanding the difference of the weights; the physical influence, if one may so express oneself, of these elements, which are so very different in their atomic weights, is almost alike.

² Therefore Berzelius called sulphur an amphoteric element. Although the analogy between the compounds of sulphur and oxygen has been recognised from the very birth of modern chemistry (the oxides and sulphides are the most widely spread metallic ores in nature), still it has only been clearly expressed by the periodic system, which places both these elements in group VI. Here, moreover, stands out that parallelism which exists between SO_2 and ozone, OO_2 , between K_2SO_3 and peroxide of potassium, K_2O_4 (Volkovitch in 1893 again drew attention to this parallelism).

crystallised, and also very often several sulphides occur combined or mixed together in these crystalline compounds. If they are yellow and have a metallic lustre they are called pyrites. Such are, for example, copper pyrites, CuFeS_2 , and iron pyrites, FeS_2 , which is the commonest of all. They are all also known as glances or blendes if they are greyish and have a metallic lustre—for example, zinc blende, lead glance, PbS , antimony glance, Sb_2S_3 , &c. And, lastly, sulphur occurs **in the free state**. It occurs in this form in the most recent geological formations in admixture with limestone and gypsum, and most frequently in the vicinity of active or extinct volcanoes. As the gases of volcanoes contain sulphur compounds—namely, sulphuretted hydrogen and sulphurous anhydride, which by reacting on each other may produce sulphur, and as also the latter frequently appears in the craters of volcanoes as a sublimate—it might be imagined that the sulphur was of volcanic origin. But on a nearer acquaintance with its mode of occurrence, and more especially considering its relation to gypsum, CaSO_4 , and limestone, the opinion most generally accepted at the present time is that the ‘native’ sulphur has been formed by the reduction of the gypsum by organic matter, and that its occurrence is only indirectly connected with volcanic agencies. Near Tetush, on the Volga, there are beds containing gypsum, sulphur, and asphalt (mineral tar). In Europe the most important deposits of sulphur are in the south of Sicily from Catania to Girgenti.³ There are very rich deposits of sulphur in Daghestan, near Cherkai, and Cherkat in Khyut, near Mount Kanabour-bam, near Petrovsk, and in the Kira Koumski steppes in the transcaspian provinces, which are able to supply the whole of Russia with this mineral. Abundant deposits of sulphur have also been found in Kamtchatka in the neighbourhood of the volcanoes. The method of separation of the sulphur from its earthy impurities is based on the fact that sulphur melts when it is heated. The fusion is carried on at the expense of a portion of the sulphur, which is burnt, so that

³ In Sicily I found, near Caltanissetta, a specimen of sulphur with mineral tar. In the same neighbourhood there are naphtha springs and mud volcanoes. It may be that these substances partly reduced the sulphur from gypsum.

The chief proof in favour of the origin of sulphur from gypsum is that in treating the deposits for the extraction of the sulphur it is found that the proportion of sulphur to calcium carbonate never exceeds that which it would be had they both been derived from calcium sulphate. As micro-organisms having the faculty of reducing and depositing sulphur from sulphates have been found in salt water, the origin of deposits of free sulphur in nature might be ascribed to their agency. Erenberg and others discovered micro-organisms (*Beggiatoa*, &c.) with granules of sulphur inside them many years ago, and Winogradsky demonstrated that they thrive in those localities where there is a supply of free sulphuretted hydrogen, from which they reduce the sulphur, which is then oxidised by the organisms to sulphuric acid.

the remainder may melt and run from the mass of the earth. This is carried on in special furnaces called *calcaroni*, built up of unhewn stone in the neighbourhood of the mines.⁴

Sulphur is purified by distillation in special retorts (see fig. 97) by passing the vapour into a chamber, G, built of stone. The first portions of the vapour entering the condensing chamber are condensed directly from the vapour into a solid state, and form a fine powder known as **flowers of sulphur**.⁵ But when the temperature of the receiver attains the melting-point of sulphur, it passes into a liquid state and is cast into moulds (like sealing-wax), and is then known under the name of **roll sulphur**.⁶

In an uncombined state sulphur exists in **several modifications**, and forms a good example of the facility with which an alteration of properties can take place without a change of composition—that is, as regards the material of a substance. Common sulphur has the well-known yellow colour. This colour fades as the temperature falls, and

⁴ Naturally only those ores of sulphur which contain a considerable amount of sulphur can be treated by this method. With poor ores it is necessary to have recourse to distillation or mechanical treatment in order to separate the sulphur; but its price is so low that this method in most cases is not profitable.

The sulphur obtained by the above-described method still contains some impurities, but it is frequently made use of in this form for many purposes, and especially in considerable quantities for the manufacture of sulphuric acid and for strewing over grapes. For other purposes, and especially in the preparation of gunpowder, a purer sulphur is required. Sulphur may be purified by distillation. The crude sulphur is called **rough**, and the distilled sulphur **refined**. The arrangement depicted in fig. 97 is employed for refining sulphur. The rough sulphur is melted in the boiler *d*, and as it melts it is run through the tube F into an iron retort, B, heated by the naked flame of the furnace. Here the sulphur is converted into vapour, which passes through a wide tube into the chamber G, surrounded by stone walls and furnished with a safety-valve, S.

⁵ Flowers of sulphur always contain a certain amount of the oxides of sulphur.

⁶ Sulphur may be extracted by various other means. It may be extracted from iron pyrites, FeS_2 , which is very widely distributed in nature. From 100 parts of iron pyrites about half the sulphur contained, namely, about 25 parts, may be extracted by heating without access of air, a lower sulphide of iron, which is more stable under the action of heat, being left behind. Alkali waste (Chap. XII.), containing calcium sulphide and gypsum, CaSO_4 , may be used for the same purpose; but native sulphur is so cheap that recourse can only be had to these sources when the calcium sulphide appears as a worthless by-product. The most simple process for the extraction of sulphur from alkali waste, in a chemical sense, consists in evolving sulphuretted hydrogen from the calcium sulphide by the action of hydrochloric acid. The sulphuretted hydrogen, when burnt, gives water and sulphurous anhydride, which reacts on fresh sulphuretted hydrogen with the separation of sulphur. The combustion of the sulphuretted hydrogen may be so conducted that a mixture of $2\text{H}_2\text{S}$ and SO_2 is straightway formed, and this mixture will deposit sulphur (Chap. XII., note 14). Gossage and Chance treat alkali waste with carbonic anhydride, and subject the sulphuretted hydrogen evolved to incomplete combustion (this is best done by passing a mixture of sulphuretted hydrogen and air, taken in the requisite proportions, over red-hot ferric oxide), by which means water and the vapour of sulphur are formed: $\text{H}_2\text{S} + \text{O} = \text{H}_2\text{O} + \text{S}$. As much as 80 per cent. of the sulphur contained in the soda refuse may be saved in this manner.

at -50° sulphur is almost colourless. It is very brittle, so that it may be easily converted into a powder, and it presents a crystalline structure, which, by the way, shows itself in the unequal expansion of lumps of sulphur by heat. Hence, when a piece of sulphur is heated by the warmth of the hand, it emits sounds, and sometimes cracks, which probably also depends on the bad heat-conducting power of this

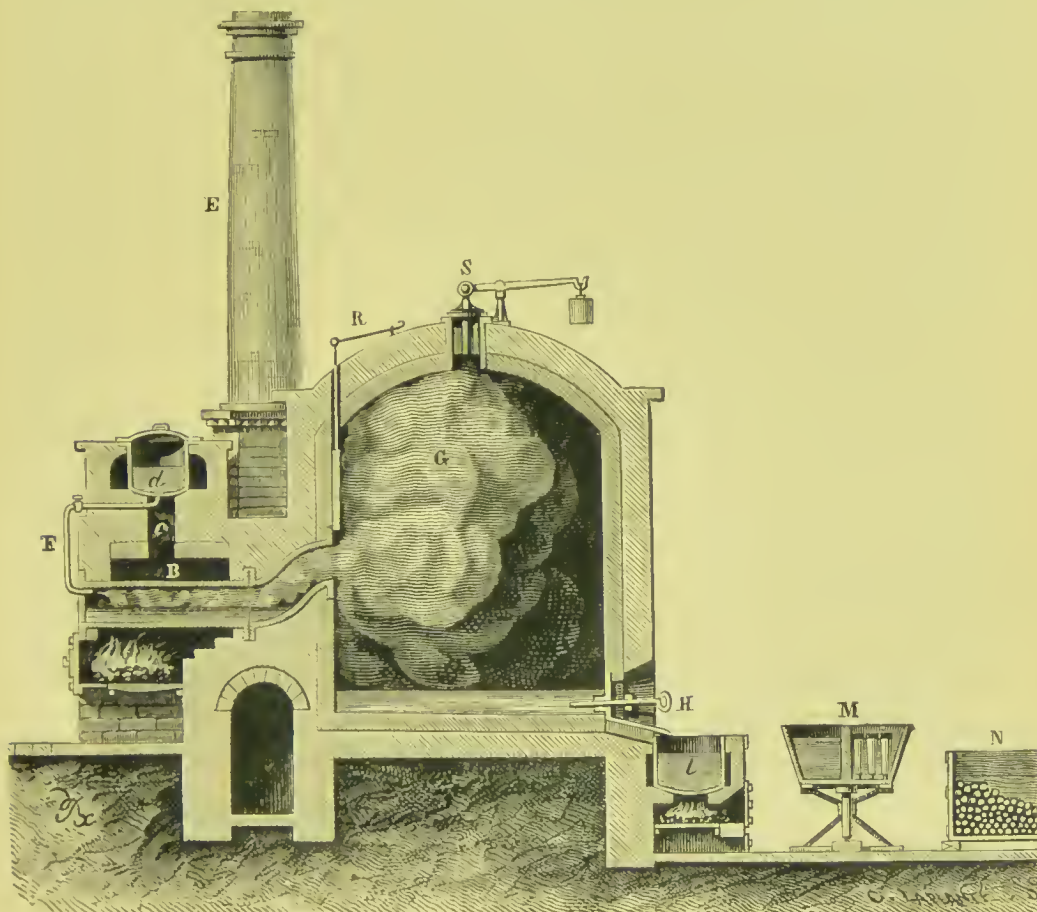


FIG. 97.—Refining sulphur by sublimation.

substance. It is easily obtained in a crystalline form by artificial means, because, although insoluble in water, it dissolves in carbon bisulphide and in certain oils.⁷ Solutions of sulphur in carbon

⁷ One hundred parts of liquid carbon bisulphide, CS_2 , dissolve 16.5 parts of sulphur at -11° , 24 parts at 0° , 37 parts at 15° , 46 parts at 22° , and 181 parts at 55° . The saturated solution boils at 55° , whilst pure carbon bisulphide boils at 47° . When sulphur is dissolved in carbon bisulphide it reduces the temperature, just as in the solution of salts in water. Thus, the solution of 20 parts of sulphur in 50 parts of carbon bisulphide at 22° lowers the temperature by 5° ; 100 parts of benzene, C_6H_6 , dissolve 0.965 part of sulphur at 26° , and 4.377 parts at 71° ; chloroform, CHCl_3 , dissolves 1.2 part of sulphur at 22° , and 16.35 parts at 174° .

bisulphide, when evaporated at the ordinary temperature, yield well-formed transparent crystals of sulphur in the form of **rhombic octahedra**, in which form it occurs native. The specific gravity of these crystals is 2.045. Fused sulphur, cast into moulds and cooled, has, after being kept a long time, a specific gravity 2.06, almost the same as that of the crystalline sulphur of the above form, which shows that common sulphur is the same as that which crystallises in octahedra. The specific heat of octahedral sulphur is 0.17; it melts at 114°, and forms a bright yellow mobile liquid. On further heating, the fused sulphur undergoes an alteration, which we shall presently describe, first observing that the above octahedral state of sulphur is its most stable form. At the ordinary temperature sulphur may be kept in this form for an indefinite length of time, and many other modifications of sulphur pass into this form after being left for a certain time at the ordinary temperature.

If sulphur is melted and then slightly cooled, so that it forms a crust on the surface and over the sides of the crucible, while the internal mass remains liquid, it then takes another crystalline form as it solidifies. This may be seen by breaking the crust and pouring out the remaining molten sulphur.⁸ It is then found that the sides of the crucible are covered with oblique **prismatic crystals** of the monoclinic system; they have an appearance totally different from that of the above-described crystals of rhombic sulphur. The prismatic crystals are brown, transparent, and less dense than the crystals of rhombic sulphur, their specific gravity being only 1.93, and their melting-point higher—about 119.3°. ^{8a} These crystals of sulphur cannot be kept at the ordinary temperature, which is indeed evident from the fact that in time they turn yellow; the specific gravity also changes, and they pass completely into the ordinary modification. This transformation is accompanied by a considerable development of heat, so that the temperature of the mass may rise as much as 12°. Thus, **sulphur is dimorphous**—that is, it exists in two crystalline forms, and in the two forms it has independent physical properties. However, no chemical reactions are known which distinguish the two modifications

⁸ Octahedral sulphur passes into the prismatic form at temperatures above 80°, as is seen from the fact that when a solution of sulphur in benzene is evaporated at temperatures higher than 80°, it leaves prismatic sulphur, while the same solution, evaporated at the ordinary temperature, deposits octahedral crystals. Also the octahedral crystals become opaque and form prismatic sulphur when heated to 90°. The latter is again transformed into octahedral sulphur at the ordinary temperature.

^{8a} A. Smith and W. Holmes (1902) showed that the observed differences in the melting-point of sulphur are due to the presence of amorphous sulphur, which ordinary sulphur contains in variable proportions.

of sulphur, just as there are none distinguishing aragonite from calc spar.⁹

If molten sulphur is heated to 160°–220°, it loses its mobility and becomes thick and very dark-coloured, so that the crucible in which it is heated may be inverted without the sulphur running out. When heated above this temperature the sulphur again becomes more liquid, and at 250°–300° it is very mobile, although it does not acquire its original colour, and at 448° it boils. These modifications in the properties of sulphur depend not only on the variations of temperature, but also on a change of structure. If sulphur, heated to about 350°, is poured in a thin stream into cold water, it does not solidify into a solid mass, but retains its brown colour and **remains soft**; it may be stretched out into threads, and is elastic, like gutta percha. But it does not remain in this soft and ductile state for a long time. After the lapse of a certain period the soft, transparent sulphur hardens, becomes opaque, passes into the ordinary yellow modification of sulphur, and in so doing develops heat, just as in the conversion of the prismatic into the octahedral variety. The soft sulphur is characterised by the fact that a certain portion of it is insoluble in carbon bisulphide. When soft sulphur is immersed in this liquid, only a portion of common sulphur passes into solution, whilst a certain portion is quite insoluble and remains so for a long time. The maximum proportion of insoluble sulphur is obtained by heating it slightly above 170°, especially in the presence of air, or when air, or SO₂ or HCl is passed through it;^{9a} it lowers the fusing-point of sulphur. An exactly similar **insoluble (amorphous) sulphur** is obtained in certain reactions in the wet way, when sulphur separates out from solutions. Thus sodium thiosulphate, Na₂S₂O₃, when treated with acids, gives a

" If sulphur be cautiously melted in a U-tube immersed in a salt bath, and then gradually cooled, it is possible for all the sulphur to remain liquid at 100°. It will now be in a state of superfusion; thus, by careful refrigeration, water may also be obtained in a liquid state at –10°, and a lump of ice then causes such water to form ice, and the temperature rises to 0. If a prismatic crystal of sulphur be thrown into one branch of the U-tube containing the liquid sulphur at 100°, and an octahedral crystal be thrown into the other branch, then, as Gernez showed, the sulphur in each branch will crystallise in the corresponding form, and both forms are obtained at the same temperature; so that it is not the influence of temperature only which causes the molecules of sulphur to distribute themselves in one or another form, but also the influence of the crystalline parts already formed. This phenomenon is essentially analogous to that of supersaturated solutions.

^{9a} A. Smith and W. Holmes (1902) found that 34–37 per cent. of amorphous sulphur are formed if these gases are passed into sulphur heated in its vapour (448°) for about 1½ hour. Not more than 5 per cent. are formed if the sulphur is heated in an atmosphere of NH₃, CO₂, H₂S, or N₂. Moreover, no amorphous sulphur at all is formed in NH₃; or, if it is formed, it is converted into the soluble variety. Smith and Holmes ascribe the molecule S₈ to amorphous sulphur.

precipitate of sulphur, which is insoluble in carbon bisulphide. The action of water on sulphur chloride also gives a similar modification of sulphur. Certain sulphides, when treated with nitric acid, also yield sulphur in this form.¹⁰

At temperatures of 448° – 700° the vapour density of sulphur is 6.6 referred to air—i.e., about 96 referred to hydrogen.^{10a} Hence at

¹⁰ A certain amount of insoluble sulphur remains for a long time in the mass of soft sulphur, changing into the ordinary variety. Freshly cooled soft sulphur contains about one-third of insoluble sulphur, and after the lapse of two years it still contains about 15 per cent. Flowers of sulphur, obtained by the rapid condensation of sulphur from a state of vapour, also contains a certain amount of insoluble sulphur. *Rapidly distilled and condensed sulphur* also contains some insoluble sulphur. Hence a certain amount of insoluble sulphur is frequently found in roll sulphur. The action of light on a solution of sulphur converts a certain portion into the insoluble modification. Insoluble sulphur is of a lighter colour than the ordinary variety. It is best prepared by vaporising sulphur in a stream of carbonic anhydride, hydrochloric acid, &c., and collecting the vapour in cold water. When condensed in this manner it is nearly all insoluble in carbon bisulphide. It then has the form of hollow spheroids, and is therefore lighter than the common variety, having the sp. gr. 1.82. An idea of the modifications taking place in sulphur between 110° and 250° may be formed from the fact that at 150° liquid sulphur has a coefficient of expansion of about 0.0005, whilst between 150° and 250° it is less than 0.0003.

Engel (1891), by decomposing a saturated solution of hyposulphite of sodium (note 42) with HCl in the cold (the sulphur is not precipitated directly in this case), obtained, after shaking up with chloroform and evaporation, crystals of sulphur (sp. gr. 2.135), which, after several hours, passed into the insoluble (in CS_2) state, and in so doing became opaque and increased in volume. But if a mixture of solutions of $\text{Na}_2\text{S}_2\text{O}_3$ and HCl is allowed to stand, it deposits sulphur, which, after sufficient washing, is able to dissolve in water (like the colloidal varieties of the metallic sulphides, alumina, boron, and silver), but this colloidal solution of sulphur soon deposits sulphur insoluble in CS_2 .

When a solution of sulphuretted hydrogen in water is decomposed by an electric current, the sulphur is deposited on the positive pole, and has therefore an electro-negative character, and this sulphur is soluble in carbon bisulphide. When a solution of sulphurous acid is decomposed in the same manner, the sulphur is deposited on the negative pole, and is therefore electro-positive, and the sulphur so deposited is insoluble in carbon bisulphide. The sulphur which is combined with metals must have the properties of the sulphur contained in sulphuretted hydrogen, whilst the sulphur combined with chlorine is like that which is combined with oxygen in sulphurous anhydride. Hence Berthelot recognises the presence of soluble sulphur in metallic sulphides, and of the insoluble modification of amorphous sulphur in sulphur chloride. Cloëz showed that the sulphur precipitated from solutions is either soluble or insoluble, according to whether it separates from an alkaline or acid solution. If sulphur is melted with a small quantity of iodine or bromine, on pouring out the molten mass it forms amorphous sulphur, which keeps so for a very long time, and is insoluble, or nearly so, in carbon bisulphide. This is taken advantage of in casting certain articles in sulphur which by this means retain their tenacity for a long time; for example, the discs of electrical machines.

^{10a} Bleyer and Cox determined the vapour density of sulphur under a low pressure, i.e., at lower temperatures, and found that it distinctly increases as the temperature falls, and gives reason for assuming that the molecule of sulphur contains 8 atoms (S_8) at low temperatures. This is all the more remarkable because the cryoscopic behaviour of solutions in benzene and molten naphthalene, according to Biltz and Herz, and the rise of boiling-point (in CS_2 by Beckmann and in CCl_4 by Odde and Serra) both indicate that in

these temperatures the molecule of sulphur contains six atoms and has the composition S_6 . The agreement between the observations of Dumas, Mitscherlich, Bineau, and Deville confirms the accuracy of this result. But in this respect the properties of sulphur were found to be variable. When heated to higher temperatures, that is to say, above 800° , the vapour density of sulphur is found to have one-third of this value, i.e., about 32 referred to hydrogen. At this temperature the molecule of sulphur, like that of hydrogen, oxygen, nitrogen, and chlorine, contains only two atoms; hence the molecular formula is then S_2 . This variation in the vapour density of sulphur evidently corresponds with polymeric change, and may be likened to the transformation of ozone, O_3 , into oxygen, O_2 , or, better still, of benzene, C_6H_6 , into acetylene, C_2H_2 .¹¹

In its faculty for combination, sulphur most closely resembles oxygen and chlorine; like them, it combines with nearly all the elements, with the development of heat and light, forming sulphur compounds, but as a rule this only takes place at a high temperature. At the ordinary temperature it does not enter into reactions, owing, with

solutions the molecule of sulphur contains 8 atoms. Hence the molecule of sulphur must now be considered to contain 8 atoms at low temperatures, 6 atoms at 400° – 600° and only 2 atoms above 800° .

¹¹ Here, however, it is very important to remark that both benzene and acetylene can exist at the ordinary temperature, whilst the sulphur molecule S_2 only exists at high temperatures; and if this sulphur is allowed to cool, it passes first into S_6 and then into a liquid state, probably S_8 , note 10a. Were it possible to have sulphur at the ordinary temperature in both the above modifications, in all probability the sulphur in the state S_2 would then present totally different properties from those which it has in the form S_6 , just as the properties of gaseous acetylene are far from being similar to those of liquid benzene. Sulphur, in the form of S_2 , is probably a substance which boils at a much lower temperature than the variety with which we are now dealing.

One must here call attention to the fact that sulphur, with all its analogy to oxygen (which also shows itself in its power to give the modification S_2), is also able to give a series of compounds containing more atoms of sulphur than the analogous oxygen compounds do of oxygen. Thus, for instance, compounds of five atoms of sulphur with 1 atom of barium, BaS_5 , are known, whereas with oxygen only BaO_2 is known. On every side one cannot but see in sulphur a faculty for the union of a greater number of atoms than with oxygen. With oxygen the form of ozone, O_3 , is very unstable, the stable form being O_2 ; whilst with sulphur, S_6 is the stable form and S_2 is exceedingly unstable. Furthermore, it is remarkable that sulphur gives a higher degree of oxidation, H_2SO_4 , corresponding, as it were, with its complex composition, if we suppose that in S_6 four atoms of sulphur are replaced by oxygen and one by two atoms of hydrogen. The formulæ of its compounds, K_2SO_4 , $K_2S_2O_8$, K_2S_5 , BaS_5 , and many others, have no analogues among the compounds of oxygen. They all correspond with the form S_6 .

But although the form O_6 is unknown for oxygen, which only gives O_3 , yet the tendency of oxygen to form complex compounds is seen in its capacity to give H_2O_2 and K_2O_4 (corresponds to Baejer's ozonic acid and $=O_3 + K_2O$, that is, as it were, a hydrate of ozone), and in the power of the hydrogen compounds of the elements to form not only compounds with O_4 (Chap. XV.), but also the higher forms of peroxides. This apparently introduces a new form of analogy between sulphur and hydrogen.

other things, to the fact that it is a solid. In a molten state it acts on most metals and on the halogens. It burns in air at about 300° , and with carbon at a red heat, but it does not combine with nitrogen.

Fine wires, or the powders of the greater number of metals, burn in the vapour of sulphur. The direct combination of hydrogen with sulphur is restricted by a limit—that is, at a given temperature and under other given conditions it does not proceed unrestrictedly; there is no explosion or recalescence. Sulphuretted hydrogen, H_2S , decomposes at its temperature of formation—that is, it is easily dissociated.¹² The same phenomenon is repeated here as with water, except that the temperatures at which the attraction of hydrogen for sulphur begins and ceases are much lower than in the case of oxygen and hydrogen. The temperature at which combination takes place is here, as in many other instances, nearly the same as that at which dissociation begins. Hence **sulphuretted hydrogen** is formed in small quantity by the direct ignition of a mixture of the vapour of sulphur and hydrogen. However, the temperature must not be high, because otherwise the whole of the sulphuretted hydrogen will be decomposed; but at lower temperatures a small amount of sulphuretted hydrogen is formed by direct combination.¹³ Sulphuretted hydrogen, however, like all other hydrogen compounds, may be easily obtained by the double decomposition of its corresponding metallic compounds, the replacement of the metal by hydrogen being effected by the action of acids on the sulphides according to the equation: $\text{M}_2\text{S} + \text{H}_2\text{SO}_4 = \text{H}_2\text{S} + \text{M}_2\text{SO}_4$. However, it is not all sulphides or solutions of all acids that will evolve sulphuretted hydrogen, which fact is exceedingly characteristic, because, for example, all carbonates evolve carbonic anhydride when treated with any acid. Sulphuric acid will only evolve sulphuretted hydrogen from those sulphides which contain a metal capable of decomposing the acid with the evolution of hydrogen. Thus zinc, iron, calcium, magnesium, manganese, potassium, sodium, &c., form sulphides which evolve sulphuretted hydrogen when treated with sulphuric acid, and the metals themselves

¹² In the formation of potassium sulphide, K_2S (that is, in the combination of 32 parts of sulphur with 78 parts of potassium), about 100 thousand heat units are developed. Nearly as much heat is developed in the combination of an equivalent quantity of sodium; about 90,000 heat units in the formation of calcium or strontium sulphide; about 40,000 for zinc or cadmium sulphide, and about 20,000 for iron, cobalt, or nickel sulphide. Less heat is evolved in the combination of sulphur with copper, lead, and silver. According to Thomsen, $\text{H}_2 + \text{S}$ develops 4,512 calories.

¹³ If sulphur is melted in a flask and heated nearly to its boiling-point, as Lidoff showed, the addition, drop by drop (from a funnel with a stopcock), of heavy (0.9) naphtha oil (of lubricating oleonaphtha), &c., is followed by a regular evolution of sulphuretted hydrogen. This is analogous to the action of bromine or iodine on paraffin and other oils, because hydrobromic or hydriodic acid is then formed (Chap. XI.). A certain amount of hydrogen sulphide is even formed when sulphur is boiled with water.

evolve hydrogen with acids.¹⁴ The sulphides of those metals which do not liberate hydrogen from acids do not generally act on acids—that is, do not form sulphuretted hydrogen with them; such are, for example, the sulphides of lead, silver, copper, mercury, tin, &c. The usual mode of preparing sulphuretted hydrogen is by the action of **sulphuric acid on ferrous sulphide**, in which the same apparatus and method are employed as in the preparation of hydrogen, only replacing the metallic iron or zinc by ferrous sulphide. The reaction is expressed by the equation: $\text{FeS} + \text{H}_2\text{SO}_4 = \text{FeSO}_4 + \text{H}_2\text{S}$.¹⁵

In nature, sulphuretted hydrogen is formed in many ways. The

¹⁴ However, the matter is really much more complicated. Thus zinc sulphide evolves sulphuretted hydrogen with sulphuric or hydrochloric acid, but does not react with acetic acid and is oxidised by nitric acid. Ferrous sulphide evolves sulphuretted hydrogen with acids, whilst the bisulphide, FeS_2 , does not react with acids of ordinary strength. This absence of action depends, among other things, on the form in which the native iron pyrites occurs; it is a crystalline, compact, and very dense substance, and acids in general react with great difficulty on such metallic sulphides. This is seen very clearly in the case of zinc sulphide; if this substance is obtained by double decomposition, it separates as a white precipitate, which evolves sulphuretted hydrogen with great ease when treated with acids. Zinc sulphide is obtained in the same form when zinc is fused with sulphur, but native zinc sulphide—which occurs in compact masses of zinc blende and has a metallic lustre—is decomposed not at all or but slightly by sulphuric acid.

Another source of complication in the behaviour of the metallic sulphides towards acids depends on the action of water, and is shown by the fact that the action varies with different degrees of dilution or proportion of water present. The best known example of this is antimonious sulphide, Sb_2S_3 , for strong hydrochloric acid, containing not more water than corresponds with $\text{HCl}, 6\text{H}_2\text{O}$, decomposes even native antimony glance, with evolution of sulphuretted hydrogen, whilst dilute acid has no action, and in the presence of an excess of water the reaction, $2\text{SbCl}_3 + 3\text{H}_2\text{S} = \text{Sb}_2\text{S}_3 + 6\text{HCl}$, occurs, whilst in the presence of a small amount of water the reaction proceeds in exactly the opposite direction. Here the participation of water in the reaction and its affinity are evident.

The facts that lead sulphide is insoluble in acids, that zinc sulphide is soluble in hydrochloric acid but insoluble in acetic acid, that calcium sulphide is even decomposed by carbonic acid, &c.—all these peculiarities of the sulphides are in correlation with the amount of heat evolved in the reaction of the oxides with hydrogen sulphide and with acids, as is seen from the observations of Favre and Silberman, and from the comparisons made by Berthelot in 1870.

¹⁵ **Ferrous sulphide** is formed by heating a piece of iron to an incipient white heat, and then removing it from the furnace and bringing it into contact with a piece of sulphur. Combination then proceeds, accompanied by the development of heat, and the ferrous sulphide formed fuses. The sulphide of iron thus formed is a black, easily fusible substance, insoluble in water. When damp it attracts oxygen from the air, and is converted into green vitriol, FeSO_4 . If all the iron does not combine with the sulphur in the method described above, the action of sulphuric acid will evolve hydrogen as well as hydrogen sulphide.

Ferrous sulphide may be advantageously replaced by calcium sulphide or a mixture of calcium and magnesium sulphides. A solution of magnesium hydrosulphide, $\text{MgS}, \text{H}_2\text{S}$, is very convenient, as at 60° it evolves a stream of pure hydrogen sulphide. A paste, consisting of CuS with crystals of MgCl_2 and water, may also be employed, since it only evolves H_2S when heated (Habermann).

most usual mode of its formation is by the decomposition of albuminous substances containing sulphur, as mentioned above. Another method is by the reducing action of organic matter on sulphates, and by the action of water and carbonic acid on the sulphides formed by this reduction. Volcanic eruptions are a third source of sulphuretted hydrogen in nature. Although sulphuretted hydrogen is formed in small quantities everywhere, it nevertheless soon disappears from the atmosphere, owing to its being easily decomposed by oxidising agencies. Many mineral waters contain sulphuretted hydrogen, and smell of it; they are called 'sulphur waters.'

Sulphuretted hydrogen, at the ordinary temperature, is a colourless gas, having a very unpleasant odour. It has, as its composition H_2S shows, a specific gravity seventeen times greater than that of hydrogen, and therefore it is somewhat heavier than air. Sulphuretted hydrogen **liquefies** at about -62° , or at the ordinary temperature when subjected to a pressure of 10 to 15 atmospheres; at -85° it is converted into a solid crystalline mass.^{15a} One volume of water at 0° dissolves 4.37 volumes of sulphuretted hydrogen; at 10° , 3.58 volumes; and at 20° , 2.9 volumes.¹⁶ The solutions impart a very feeble red coloration to litmus paper. This gas is poisonous. One part in fifteen hundred parts of air will kill birds. Mammalia die in an atmosphere containing $\frac{1}{200}$ part of this gas.

Sulphuretted hydrogen is very easily **decomposed** into its component parts by the action of heat or of a series of electric sparks.^{16a} Hence it is not surprising that sulphuretted hydrogen undergoes change under the action of many substances having a considerable affinity for hydrogen and oxygen. Very many metals¹⁷ evolve hydrogen with sulphuretted

^{15a} Liquid sulphuretted hydrogen is most easily obtained by the decomposition of hydrogen polysulphide, which we shall presently describe, by the action of heat and in the presence of a small amount of water. If poured into a bent tube, like that described for the liquefaction of ammonia (Chap. VI.), the hydrogen polysulphide is decomposed by heat, in the presence of water, into sulphur and sulphuretted hydrogen, which condenses in the cold end of the tube into a colourless liquid.

¹⁶ Sulphuretted hydrogen is still more soluble in alcohol than in water; one volume of the former at the ordinary temperature dissolves as much as eight volumes of the gas. The solutions in water and alcohol undergo change, especially in open vessels, owing to the fact that the water and alcohol dissolve oxygen from the atmosphere, which, acting on the sulphuretted hydrogen, forms water and sulphur. The solution may be so altered in this manner that every trace of sulphuretted hydrogen disappears. Solutions of sulphuretted hydrogen in glycerine change much more slowly, and may therefore be kept for a long time as reagents. De Forcrand obtained a hydrate, $\text{H}_2\text{S} \cdot 16\text{H}_2\text{O}$, resembling the hydrates given by many other gases.

^{16a} Hautefeuille observed not only the formation of H_2S from sulphur and hydrogen, but also the decomposition of H_2S at 400° , and Konovaloff observed the formation at 310° , but decomposition did not take place at that temperature.

¹⁷ Some metals evolve hydrogen from sulphuretted hydrogen at the ordinary tem-

hydrogen, so that in this respect it presents the property of an acid ; for instance, $2\text{H}_2\text{S} + \text{Sn} = 2\text{H}_2 + \text{SnS}_2$. This may be taken advantage of for determining the composition of sulphuretted hydrogen, because a given volume then leaves the same volume of hydrogen. On the other hand, oxygen,¹⁸ chlorine,¹⁹ or even iodine decomposes sulphuretted hydrogen, removing the hydrogen from it and leaving free sulphur, so that in this reaction the sulphur is replaced by the above-named elements ; for example, $\text{H}_2\text{S} + \text{Br}_2 = 2\text{HBr} + \text{S}$. In no other hydrogen compound is it so easy to show the **substitution**, both of hydrogen and of the element combined with it, as in hydrogen sulphide. This clearly proves the feeble union between the elements forming this gas. Oxidising agents accomplish the separation of the sulphur very easily ; for instance, nitrous acid, chromic acid, and even ferric oxide and the higher oxides like it. Thus, if sulphuretted hydrogen is passed into a solution of chromic acid or an acid solution of ferric oxide, water is formed, and the sulphur is separated in a free state. Thus, sulphuretted hydrogen acts as a **reducing agent** in virtue of the hydrogen it contains. In the presence of an excess of a powerful oxidising agent a portion of the sulphur may also be oxidised and form sulphuric acid. The reducing action of sulphuretted hydrogen is frequently applied in chemical manipulations for the preparation of lower oxides and for the conversion of certain oxygen compounds into hydrogen compounds ; the higher oxides of nitrogen are converted into ammonia, and in the presence of alkalis the nitro-compounds are converted into ammonia derivatives, &c. The action of sulphuretted hydrogen on sulphurous anhydride belongs to this class of phenomena, the chief products being sulphur and water, $2\text{H}_2\text{S} + \text{SO}_2 = 2\text{H}_2\text{O} + \text{S}_3$.

The acid character of sulphuretted hydrogen is clearly seen in its action on alkalis and salts.^{19a} Thus, lead oxide and its salts, in the presence of sulphuretted hydrogen, form water or an acid, and sulphide of lead : $\text{PbX}_2 + \text{H}_2\text{S} = \text{PbS} + 2\text{HX}$. This reaction takes place

perature. For example, the light metals, and copper and silver (especially with access of air?) among the heavy metals. Hence articles made of silver turn black in the presence of vapours containing sulphuretted hydrogen, because silver sulphide is black. Zinc and cadmium act at a red heat, but not completely.

¹⁸ If sulphuretted hydrogen escapes from a fine orifice into the air, it will burn when lighted, and will be transformed into sulphurous anhydride and water. But if it burns in a limited supply of air—for instance, when a cylinder is filled with it and lighted—then only the hydrogen burns, which has, judging from the amount of heat developed in its combustion and from all its properties, a greater affinity for oxygen than sulphur. In this respect the combustion of sulphuretted hydrogen resembles that of hydrocarbons.

¹⁹ Hence bleaching powder and chlorine destroy the disagreeable smell of sulphuretted hydrogen. (For the reaction of hydrogen sulphide and iodine, see Chap. XI.)

^{19a} Perfectly dry H_2S (Hughes, 1892) has no action upon perfectly dry salts, just as dry HCl does not react with dry NH_3 or metals (Chap. IX., note 29).

even in the presence of powerful acids, because lead sulphide is one of those sulphides which are unacted on by acids, and in solutions the reaction is a complete one. This reaction is taken advantage of for the preparation of many acids, by first converting into a lead salt, and then submitting this salt to the action of sulphuretted hydrogen. For example, lead formate with sulphuretted hydrogen gives formic acid. Sulphuretted hydrogen in acting on a number of metallic acid substances in solution or in an anhydrous state also forms corresponding sulphates : (1) if it does not reduce the acid ; (2) if the sulphur compound corresponding with the anhydride of the acid is insoluble in water, the reaction proceeds in solutions ; (3) if the sulphuretted hydrogen and the acid taken do not come into contact with an alkali, on which they would be able to act first ; and (4) if the sulphur compound is not decomposed by water. Thus, solutions of arsenious acid give a precipitate of arsenious sulphide, As_2S_3 , with sulphuretted hydrogen. This reaction proceeds in the presence not only of water, but also of acids, because the latter do not decompose the resultant sulphur compounds. The type of the decomposition is the same as with bases—that is, the sulphur and oxygen change places : $\text{RO}_n + n\text{H}_2\text{S} = \text{RS}_n + n\text{H}_2\text{O}$. Some sulphides corresponding with acid anhydrides are decomposed by water, and therefore are not formed in the presence of water. Such, for example, are the sulphides of phosphorus.²⁰

²⁰ The sulphide P_3S is obtained by cautiously fusing the requisite proportions of common phosphorus and sulphur under water ; it is a liquid which solidifies at 0° , and may be distilled without undergoing change, but it fumes in air and easily takes fire. The higher sulphide, P_2S , has similar properties. But little heat is evolved in the formation of these compounds, and it may be supposed that they are formed by the direct conjunction of whole molecules of phosphorus and sulphur ; but if the proportion of sulphur be increased, the reaction is accompanied by so considerable a rise of temperature that an explosion takes place, and for the sake of safety red phosphorus must be used, mixed as intimately as possible with powdered sulphur and heated in an atmosphere of carbonic anhydride. The higher compounds are decomposed by water. By increasing the proportion of sulphur, the following compounds have been obtained : P_4S_3 as prisms (fusing at 165° , Rebs), soluble in carbon bisulphide, and unaltered by air and water ; **phosphorus trisulphide**, P_2S_3 , the analogue of P_2O_3 , is a light-yellow crystalline compound only slightly soluble in carbon bisulphide ; it is fusible and volatile, is decomposed into hydrogen sulphide and phosphorous acid by water, and, like the highest compound of sulphur and phosphorus, P_2S_5 , forms thio-salts with potassium sulphide, &c. This **phosphorus pentasulphide** corresponds with phosphoric anhydride ; like the trisulphide, it gives hydrogen sulphide and phosphoric acid with an excess of water. It reacts in many respects like phosphoric chloride. The sulphide PS_2 is also known ; the vapour density of this compound seems to indicate a molecule, P_3S_6 .

Phosphorus sulphochloride, PSCl_3 , corresponds with phosphorus oxychloride. It is a colourless, pleasant-smelling liquid, boiling at 124° , and of sp. gr. 1.63 ; it fumes in air and is decomposed by water : $\text{PSCl}_3 + 4\text{H}_2\text{O} = \text{PH}_3\text{O}_4 + \text{H}_2\text{S} + 3\text{HCl}$. It is obtained when phosphoric chloride is treated with hydrogen sulphide, hydrochloric acid being also formed ; it is also produced by the action of phosphoric chloride on certain sulphides—for example, on antimonious sulphide, also by the (cautious) action of phosphorus on sulphur

The metallic sulphides corresponding with the metallic oxides have either a feeble alkaline or a feeble acid character, according to the character of the corresponding oxide, and therefore by combining together they are able to form saline substances—that is, salts in which the oxygen is replaced by sulphur. Thus sulphuretted hydrogen, having the properties of a feeble acid,²¹ has, at the same time, the properties of water, and forms the type of the sulphurous or thio-derivatives, which may also be formed by means of sulphuretted hydrogen, just as the oxides may be formed by the aid of water. But as sulphuretted hydrogen has acid properties, it combines more easily with the basic metallic sulphides. Hence, for instance, there exists a compound of sulphuretted hydrogen with potassium sulphide, potassium hydrosulphide, $2\text{KHS} = \text{K}_2\text{S} + \text{H}_2\text{S}$, just as there are potassium hydroxides; but there are scarcely any compounds of sulphuretted hydrogen with the sulphides corresponding with acids. Thus the sulphides of the metals may be regarded either as salts of sulphuretted hydrogen or as oxides of the metals in which the oxygen is replaced by sulphur. In general terms, the sulphides exhibit the same degrees of difference with respect to their solubility in water as do the oxides. Thus, the oxides of the alkali metals and of some of the metals of the alkaline earths, are soluble in water, whilst those of nearly all the other metals are insoluble. Those metals, like aluminium, whose oxides—for example, Al_2O_3 —have intermediate properties and do not form compounds with feeble acids, at least in a wet way, also do not form sulphides by this method, although these may be obtained indirectly. And in general the sulphides of the metals are easily formed in a wet way, and with particular ease if they are insoluble in water. In this case their salts enter into double decomposition with

chloride: $2\text{P} + 3\text{S}_2\text{Cl}_2 = 2\text{PSCl}_3 + 4\text{S}$; by the action of PCl_5 upon certain sulphides, for example, Sb_2S_3 ; by the reaction: $3\text{MCl} + \text{P}_2\text{S}_5 = \text{PSCl}_3 + \text{M}_3\text{PS}_4$ (Glatzel, 1893), and in the reaction, $3\text{PCl}_3 + \text{SOCl}_2 = \text{PCl}_5 + \text{POCl}_3 + \text{PSCl}_3$, showing the reducing action of phosphorus trichloride, which is especially clear in the reaction, $\text{SO}_3 + \text{PCl}_3 = \text{SO}_2 + \text{POCl}_3$. Thorpe and Rodger (1889), by heating 3PbF_2 or BiF_3 with phosphorus pentasulphide (and also by heating AsF_3 and PSCl_3 to 150°), obtained thiophosphoryl fluoride as a colourless, spontaneously inflammable gas (see further on, note 74a, and Chap. XIX. note 25). The action of PSCl_3 upon NaHO gives a salt of *monothiophosphoric acid* (Würtz, Kubierschky), H_3PSO_3 , which yields soluble salts with alkalis.

²¹ Sulphuretted hydrogen does not saturate the alkaline properties of alkali hydroxides, so that a solution of potassium hydroxide will not under any circumstances give a neutral liquid with sulphuretted hydrogen. Sulphuretted hydrogen forms in solution only an acid salt with the potassium: $\text{KHO} + \text{H}_2\text{S} = \text{KHS} + \text{H}_2\text{O}$, but not K_2S . Furthermore, it must be taken into account that potassium oxide, K_2O , and the anhydrous oxides like it, do not exist in solutions, for whenever they are formed they immediately react with the water, forming caustic potash, KHO , &c. In the same way, directly potassium sulphide, K_2S , is formed in water it is decomposed into potassium hydroxide and hydrosulphide: $\text{K}_2\text{S} + \text{H}_2\text{O} = \text{KHO} + \text{KHS}$ (see note 27).

sulphuretted hydrogen, or with soluble sulphides, and give an insoluble sulphide—for instance, a salt of lead gives lead sulphide with sulphuretted hydrogen. By the action of sulphuretted hydrogen on a salt of a metal, a free acid must be formed besides the metallic sulphide. Thus if a metal M be in a state of combination MX_2 , then by the action of sulphuretted hydrogen there will be formed, besides MS ,²² an acid $2HX$. It is evident that sulphuretted hydrogen will not precipitate an insoluble sulphide from the salts of those metals whose sulphides react with free acid, such as zinc, iron, manganese, &c. The reaction, $FeCl_2 + H_2S = FeS + 2HCl$, and the like, do not take place, because the acid acts on the ferrous sulphide. Antimonious sulphide is not acted on by dilute hydrochloric acid, but it is decomposed by strong acid, and therefore, in presence of an excess of hydrochloric acid, antimonious chloride does not entirely react with hydrogen sulphide, whilst the reaction, $2SbCl_3 + 3H_2S = Sb_2S_3 + 6HCl$, is a complete one in a dilute solution and with a small quantity of acid. Those metallic sulphides which are decomposed by acids may be obtained in a wet way by the double decomposition of the salts of the metals, not with hydrogen sulphide, but with soluble metallic sulphides, such as sulphide of ammonium or of potassium, because then no free acid is formed, but a salt of the metal (potassium or ammonium) which was taken as a soluble sulphide. Thus, for example, $FeCl_2 + K_2S = FeS + 2KCl$.²³

²² During recent years (beginning with Schulze, 1882) it has been found that many metallic sulphides which were considered totally insoluble do, under certain circumstances, form very unstable solutions in water, as already mentioned in Chap. I., note 57. Arsenic sulphide is very easily obtained in the form of a solution (hydrosol). Solutions of copper and cadmium sulphides may also be easily obtained by precipitating their salts, CuX_2 , or CdX_2 , with ammonium sulphide and washing the precipitate; but they are reprecipitated by the addition of foreign salts.

²³ In reality the preceding reaction should be expressed thus: $FeCl_2 + 2KHS = FeS + 2KCl + H_2S$ (note 21), because in the presence of water not K_2S but KHS reacts. But as the sulphuretted hydrogen takes no part in the reaction, it is usual to express the formation of such sulphides without taking the hydrogen sulphide proceeding from the potassium or ammonium hydrosulphides into account. It is not usual to employ potassium sulphide but ammonium sulphide—or, to speak more accurately, ammonium hydrosulphide—in order to avoid the formation of a non-volatile salt of potassium and to have, together with the sulphide formed, a salt of ammonium which can always be driven off by evaporating the solution and igniting the residue. Thus the metallic sulphides may be divided into three chief classes: (1) those soluble in water, (2) those insoluble in water but reacting with acids, and (3) those insoluble in both water and acids. The third class may be easily subdivided into two groups: to the first group belong those sulphides which correspond with bases or basic oxides, and are therefore unable to play the part of an acid with the sulphides of the alkalis, and are insoluble in NH_4HS , whilst the sulphides of the second group are of an acid character, and give soluble thio-salts with the sulphides of the alkaline metals, in which they play the part of an acid. To this group belong those metals whose corresponding oxides have acid properties. It must be observed, however, that not all metallic acids have corresponding sulphides, partly owing to the fact that certain acids are reducible by sulphuretted hydrogen, especially

Metallic sulphides may be obtained by many other means besides the action of sulphuretted hydrogen on salts and oxides, or by the simple combination of metals with sulphur when heated or fused. Thus, they may also be formed by the reduction of sulphates either by heating them with charcoal or by other means. Charcoal takes up the oxygen from many sulphates, leaving corresponding sulphides. Thus sodium sulphate, Na_2SO_4 , when heated with charcoal, forms sodium sulphide, Na_2S . Besides which, metallic sulphides are also obtained by heating metals or their oxides in the vapours of many sulphur compounds—for example, in the vapour of carbon bisulphide, CS_2 , when the carbon takes up the oxygen and the sulphur combines with the

when their lower degrees of oxidation are of a basic character. Such are, for instance, the acids of chromium, manganese, &c. Sulphuretted hydrogen converts them into lower oxides, having the properties of bases. Those bases which do not combine with feeble acids, such as carbonic acid and hydrogen sulphide, give a precipitate of hydroxide with ammonium sulphide; for example, aluminium salts react in this manner. This difference of the metals in their behaviour towards sulphuretted hydrogen gives a very valuable means of separating them from each other, and is taken advantage of in analytical chemistry. If, for instance, the metals of the first and third groups occur together, it is only necessary to convert them into soluble salts, and to act on the solution of the salts with sulphuretted hydrogen; this will precipitate the metals of the third group in the form of sulphides, whilst the metals of the first group will not be in the least acted on. Such a method of separating the metals is considered more fully in analytical chemistry, and we shall therefore limit ourselves here to pointing out to which groups the most common metals belong, and the colour which is proper to the sulphide precipitated.

Metals which are precipitated by sulphuretted hydrogen, as sulphides from a solution of their salts, even in the presence of free acid :

The precipitate is soluble in ammonium sulphide :

<i>Platinum</i> (dark brown)		<i>Antimony</i> (orange)
<i>Gold</i> (dark brown)		<i>Arsenic</i> (yellow)
<i>Tin</i> (yellow and brown)		

The precipitate is insoluble in ammonium sulphide :

<i>Copper</i> (black)		<i>Mercury</i> (black)
<i>Silver</i> (black)		<i>Lead</i> (black)
<i>Cadmium</i> (yellow)		

Metals which are precipitated by ammonium sulphide from neutral solutions, but not precipitated from acid solutions by sulphuretted hydrogen :

The sulphide precipitated is soluble in hydrochloric acid :

<i>Zinc</i> (white)		<i>Manganese</i> (rose colour)		<i>Iron</i> (black)
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The sulphide precipitated is not soluble in dilute hydrochloric acid :

<i>Nickel</i> (black)		<i>Cobalt</i> (black)
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A hydroxide, and not a sulphide, is precipitated :

<i>Chromium</i> (green)		<i>Aluminium</i> (white)
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The metals of the alkalis and of the alkaline earths are not precipitated by either sulphuretted hydrogen or ammonium sulphide. The metals of the alkaline earths when in acid solutions in the form of phosphates and many other salts are precipitated by ammonium sulphide, because the latter neutralises the free acid, with formation of an ammonium salt of the acid and evolution of sulphuretted hydrogen.

metal. The sulphides formed in this manner are often crystalline, and often appear with those properties and in that crystalline form in which they occur in nature. Besides which, we must mention that many of the sulphides of the metals are oxidised in air at the ordinary, and especially at a higher, temperature, forming either SO_2 and the oxide of the metal or sulphates. This oxidation preceeds with particular ease, even at the ordinary temperature, when a metallic sulphide is precipitated from its solutions as a fine powder containing water. The sulphides of iron and manganese, &c., are very easily oxidised in this manner. But if these hydrates are ignited, they lose their water (the ignition must be carried on in a stream of hydrogen to prevent their oxidation during the process), become denser, and are no longer oxidised at the ordinary temperature. Those sulphides whose corresponding sulphates are decomposed by heat part with their sulphur in the form of sulphurous anhydride when they are ignited in air, and the metal, as a rule, remains behind as oxide. This is taken advantage of in the treatment of sulphurous ores. The process is called **roasting**.

Hydrogen not only forms sulphuretted hydrogen with sulphur, but also combines with it in several other proportions, just as it does with oxygen, forming not only water but also hydrogen peroxide. Moreover, these **polysulphides of hydrogen** are unstable, like hydrogen peroxide, and are also obtained from the corresponding polysulphides of the metals of the alkaline earths, just as hydrogen peroxide is obtained from barium peroxide. Thus, calcium forms not only calcium sulphide, CaS , but also bi-, tri-, and penta-sulphides, CaS_5 , and all these compounds are soluble in water. Sodium also forms sulphides from Na_2S to Na_2S_5 . If an acid is added to a solution of a polysulphide, it gives sulphur, sulphuretted hydrogen, and a salt of the metal. For instance, $\text{MS}_5 + 2\text{HCl} = \text{MCl}_2 + \text{H}_2\text{S} + 4\text{S}$. If we reverse the operation, and pour a solution of a polysulphide into an acid, sulphur is not precipitated, but an oily liquid is formed which is heavier than water and insoluble in it. This is the polysulphide of hydrogen: $\text{MS}_5 + 2\text{HCl} = \text{MCl}_2 + \text{H}_2\text{S}_5$. As was shown by Rebs (1888), whatever polysulphide of sodium is taken, it always gives one and the same **hydrogen pentasulphide**²⁴ of specific gravity 1.71 (15°). It can only

²⁴ Rebs took di-, tri-, tetra-, and penta-sulphides of sodium, potassium, and barium, which he prepared by dissolving sulphur in solutions of the normal sulphides; on adding hydrochloric acid he always obtained hydrogen pentasulphide, whence it is evident that $4\text{H}_2\text{S}_n = (n-1)\text{H}_2\text{S}_5 + (5-n)\text{H}_2\text{S}$. For example, if H_2S_2 were formed, it would decompose according to the equation, $4\text{H}_2\text{S}_2 = \text{H}_2\text{S}_5 + 3\text{H}_2\text{S}$. The hydrogen pentasulphide formed breaks up into hydrogen sulphide and sulphur when brought into contact with water. Previous to Rebs's researches many chemists stated that all polysulphides gave the bisulphide H_2S_2 , and Hofmann recognised only hydrogen trisulphide, H_2S_3 .

be preserved in the absence of water and at low temperatures, and then not for long: for, especially in the presence of alkalis and when slightly warmed, it splits up very easily into sulphuretted hydrogen and sulphur.²⁵

The soluble sulphides and polysulphides of the metals of the alkalis and alkaline earths — for example, of ammonium,²⁶

²⁵ The formation of the polysulphides of hydrogen, H_2S_n , is easily understood, like that of the saturated hydrocarbons, C_nH_{2n+2} , from the law of substitution, knowing that sulphur gives H_2S , because the molecule of sulphuretted hydrogen may be divided into H and HS. This radicle HS is equivalent to H. By substituting this radicle for hydrogen in H_2S we obtain $(HS)HS = H_2S_2$, $(HS)(HS)S = H_2S_3$, &c., so that the compounds represented by H_2S_n forms homologues of H_2S . The question arises why in H_2S_n the apparent limit of n is 5—that is, why does the substitution end with the formation of H_2S_5 ? The answer appears to me to be clearly because in the molecule of sulphur, S_6 , there are six atoms of sulphur (note 11). The forces in the one and the other case are the same. In the one case they hold S_6 together, in the other S_5 and H_2 ; and, judging from H_2S , the two atoms of hydrogen are equal in power and significance to the atom of sulphur. Just as hydrogen peroxide, H_2O_2 , expresses the composition of ozone, O_3 , in which O is replaced by H_2 , so also H_2S_5 corresponds with S_6 .

²⁶ **Ammonium sulphide**, $(NH_4)_2S$, may be prepared by passing sulphuretted hydrogen into a vessel full of dry ammonia, or by passing the two dry gases together into a very cold receiver. In the latter case it is necessary to prevent the access of air, and to have an excess of ammonia. Under these circumstances, two volumes of ammonia combine with one volume of sulphuretted hydrogen, and form a colourless, very volatile, crystalline substance, which has an unpleasant odour, and is very poisonous and exceedingly unstable. When exposed to the air it absorbs oxygen and acquires a yellow colour, and then contains oxygen and polysulphide compounds (because a portion of the hydrogen sulphide gives water and sulphur). It is soluble in water and forms a colourless solution, which, however, in all probability contains free ammonia and the acid salt—that is, ammonium hydrosulphide, NH_4HS , or $(NH_4)_2S \cdot H_2S$. This salt is formed when dry ammonia is mixed with an excess of dry sulphuretted hydrogen. The compound contains equal volumes of the components, $NH_3 + H_2S = (NH_4)HS$. It crystallises in an anhydrous state in colourless plates, and may be easily volatilised (dissociating, like ammonium chloride), even at the ordinary temperature; it has an alkaline reaction, absorbs oxygen from the air, is soluble in water, and its solution is usually prepared by saturating an aqueous solution of ammonia with sulphuretted hydrogen.

A solution of ammonium sulphide is able to dissolve sulphur, and then contains compounds of hydrogen polysulphide and ammonia. Some of these compounds may be obtained in a crystalline form. Thus Fritzsche obtained a compound of ammonia with hydrogen pentasulphide, or **ammonium pentasulphide**, $(NH_4)_2S_5$, in the following manner: He saturated an aqueous solution of ammonia with sulphuretted hydrogen, added powdered sulphur to it, and passed ammonia gas into the solution, which then absorbed a fresh amount. After this he again passed sulphuretted hydrogen into the solution and then added sulphur, and then again ammonia. After repeating this several times, orange-yellow crystals of $(NH_4)_2S_5$ separated out from the liquid. These crystals melted at 40° to 50° , and were very unstable.

When a solution of ammonium hydrosulphide, prepared by saturating a solution of ammonia with sulphuretted hydrogen, is exposed to the air, it turns yellow, owing to the presence of an ammonium polysulphide, whose formation is due to the sulphuretted hydrogen being oxidised by the air and converted into water and sulphur, which is dissolved by the ammonium sulphide. In certain analytical reactions it is usual to employ a solution of ammonium sulphide which has been kept for some time and has acquired a yellow colour. This yellow sulphide of ammonium deposits sulphur when saturated with

potassium,²⁷ and calcium²⁸—have the appearance and properties of salts,

acids, whilst a freshly prepared solution only evolves sulphuretted hydrogen. The yellow solution furthermore contains ammonium thiosulphate, which is derived not only from the oxidation of the ammonium sulphide, but also from the action of the liberated sulphur on the ammonia, just as an alkaline salt of thiosulphuric acid and a sulphide are formed by the action of sulphur on a solution of a caustic alkali.

²⁷ **Potassium sulphide**, K_2S , is obtained by heating a mixture of potassium sulphate and charcoal to a red heat. It may be prepared in solution by taking a solution of potassium hydroxide, dividing it into two equal parts, and saturating one portion with sulphuretted hydrogen so long as it is absorbed. This portion will then contain the acid salt, KHS (note 21). The two portions are then mixed together, when potassium sulphide is obtained in the solution. This solution has a strongly alkaline reaction, and is colourless when freshly prepared, but it very easily undergoes change when exposed to the air, forming potassium thiosulphate and polysulphides. When the solution is evaporated at low temperatures under the receiver of an air-pump, it yields crystals of the composition $K_2S, 5H_2O$ (heated at 150° , they part with 3 mol. H_2O , and at higher temperatures they lose nearly all their water without evolving sulphuretted hydrogen). When they are ignited in glass vessels they corrode the glass. When a solution of caustic potash, completely saturated with sulphuretted hydrogen, is evaporated under the receiver of an air-pump, it forms colourless rhombohedra of hydrated **potassium hydrosulphide**, $2(KHS), H_2O$ (Schöne). These crystals are deliquescent in the air, but do not change in a vacuum when heated up to 170° , and at higher temperatures they lose water but do not evolve sulphuretted hydrogen. The anhydrous compound, KHS , fuses at a dark-red heat into a very mobile yellow liquid, which gradually becomes darker in colour and solidifies to a red mass. It is remarkable that when a solution of the compound KHS is boiled it somewhat easily evolves half its sulphuretted hydrogen, leaving potassium sulphide, K_2S , in solution; and a solution of the latter in water is also able to evolve sulphuretted hydrogen on prolonged boiling, but the evolution cannot be rendered complete, so that at a certain temperature a solution of potassium sulphide will not be capable of absorbing sulphuretted hydrogen at all. From this we must conclude that potassium hydroxide, water, and sulphuretted hydrogen form a system whose complex equilibrium is subject to the laws of dissociation and depends on the relative mass of each substance, on the temperature, and on the dissociation pressures of the component elements. Potassium sulphide is soluble not only in water, but also in alcohol.

Berzelius showed that in addition to potassium sulphide there also exist potassium bisulphide, K_2S_2 ; trisulphide, K_2S_3 ; tetrasulphide, K_2S_4 ; and pentasulphide, K_2S_5 . According to the researches of Schöne, the last three are the most stable. These different compounds of potassium and sulphur may be prepared by fusing potassium hydroxide or carbonate with an excess of sulphur in a porcelain crucible in a stream of carbonic anhydride. At about 600° potassium pentasulphide is formed. When heated to 800° it loses one-fifth of its sulphur and gives the tetrasulphide, which at this temperature is stable. At a bright-red heat—namely, about 900° —the trisulphide is formed. This compound may also be formed by igniting potassium carbonate in a stream of carbon bisulphide, in which case a compound, K_2CS_3 , corresponding to potassium carbonate, is first formed and carbonic anhydride evolved. On further ignition, this compound splits up into carbon and potassium trisulphide, K_2S_3 . The tetrasulphide may also be obtained in solution if a solution of potassium sulphide be boiled with the requisite amount of sulphur without access of air. This solution yields red crystals of the composition $K_2S_4, 2H_2O$ when it is evaporated in a vacuum. These crystals are very hygroscopic, easily soluble in water, but very sparingly so in alcohol; when ignited they give off water, sulphuretted hydrogen, and sulphur. If a solution of potassium sulphide is boiled with an excess of sulphur it forms the pentasulphide, which is, however, decomposed on prolonged boiling into sulphuretted hydrogen and potassium thiosul-

²⁸ See p. 247.

whilst the sulphides of the heavy metals resemble their oxides and have

phatic : $\text{K}_2\text{S}_3 + 3\text{H}_2\text{O} = \text{K}_2\text{S}_2\text{O}_3 + 3\text{H}_2\text{S}$. A substance called **liver of sulphur** was formerly frequently used in chemistry and medicine. Under this name is known the substance which is formed by boiling a solution of caustic potash with an excess of flowers of sulphur. This solution contains a mixture of potassium pentasulphide and thiosulphate, $6\text{KHO} + 12\text{S} = 2\text{K}_2\text{S}_5 + \text{K}_2\text{S}_2\text{O}_3 + 3\text{H}_2\text{O}$. The substance obtained by fusing potassium carbonate with an excess of sulphur was also known as liver of sulphur. The sulphides of sodium, for example, Na_2S , NaHS , &c., in many respects closely resemble the corresponding potassium compounds.

²⁸ The metals of the alkaline earths, like those of the alkalis, form several compounds with sulphur; thus calcium forms compounds with one and with five atoms of sulphur. There are doubtless also intermediate sulphides. If sulphuretted hydrogen is passed over ignited lime, it forms water and **calcium sulphide**, which may also be formed by heating calcium sulphate with charcoal, whilst if sulphur is heated with lime or with calcium carbonate, oxygen compounds (calcium thiosulphate and sulphate) are naturally formed at the same time as calcium sulphide. The prolonged action of the vapour of carbon bisulphide, especially when mixed with carbonic anhydride, on strongly ignited calcium carbonate converts it completely into sulphide. Calcium sulphide is generally obtained as an almost colourless, opaque, brittle mass, which is infusible at a white heat, and is soluble in water. The act of solution (as with K_2S , note 22) is partly accompanied by a double decomposition with the water. When heated, dry calcium sulphide does not absorb oxygen from the air. An excess of water decomposes it, like many other metallic sulphides, precipitating lime (as a product of the decomposition the lime hinders the action of the water upon the CaS ; see soda refuse, Chap. XII., note 12), and forming a hydrosulphide, CaH_2S_2 , in solution. This compound is also formed by passing sulphuretted hydrogen through an aqueous solution of calcium sulphide or lime. Its solution has an alkaline reaction. It decomposes when evaporated, and absorbs oxygen from the air. **Calcium pentasulphide**, CaS_5 , is not known in a pure state, but may be obtained in admixture with calcium thiosulphate by boiling a solution of lime or calcium sulphide with sulphur : $3\text{CaH}_2\text{O}_2 + 12\text{S} = 2\text{CaS}_5 + \text{CaS}_2\text{O}_3 + 3\text{H}_2\text{O}$. A similar compound in an impure form is formed by the action of air on alkali waste, and is used for the preparation of thiosulphates.

Many of the sulphides of the metals of the alkaline earths are phosphorescent—that is, they have the faculty of **emitting light in the dark**, after having been subjected to the action either of sunlight or of any bright source of light. The luminosity lasts some time, but is not permanent and gradually disappears. This phosphorescent property is inherent, in a greater or less degree, to nearly all substances (Becquerel), but for a very short time; whilst with calcium sulphide it is comparatively durable, lasting for several hours, and Dewar (1894) showed that it is far more intense at very low temperatures (for instance, in bodies cooled in liquid oxygen to -182°). It is due to the excitation of the surfaces of substances by the action of light, and is determined by those rays which exhibit a chemical action. Hence daylight or the light of burning magnesium acts more powerfully than the light of a lamp. According to the observations of Becquerel, the presence of compounds of manganese, bismuth, sodium sulphide (but not potassium sulphide), &c., although in minute traces, is absolutely indispensable. This gives reason for thinking that the formation and decomposition of double salts perhaps form the chemical cause of the phenomena. Compounds of strontium and barium have this property to an even greater extent than calcium sulphide. These compounds may be prepared as in the following example: A mixture of sodium thiosulphate and strontium chloride is prepared; a double decomposition takes place between the salts, and, on the addition of alcohol, strontium thiosulphate, SrS_2O_3 , is precipitated, which, when ignited, leaves strontium sulphide behind. The strontium sulphide thus prepared emits (when dry) a greenish-yellow light. It contains a certain amount of sulphur, sodium sulphide, and strontium sulphate. By ignition at various temperatures, and by different methods of preparation, it is possible to obtain mixtures which emit different coloured lights.

not at all the appearance of salts, and this is more especially the case with regard to the crystalline forms in which they frequently occur in nature.²⁹

²⁹ As examples, we shall describe the sulphides of arsenic, antimony, and mercury. Arsenic trisulphide, or **orpiment**, As_2S_3 , occurs native, and is obtained pure when a solution of arsenious anhydride in the presence of hydrochloric acid comes into contact with sulphuretted hydrogen (there is no precipitate in the absence of free acid). A beautiful yellow precipitate is then obtained: $\text{As}_2\text{O}_3 + 3\text{H}_2\text{S} = 3\text{H}_2\text{O} + \text{As}_2\text{S}_3$; it fuses when heated, and volatilises without decomposition. As_2S_3 is easily obtained in a colloidal form (Chap. I., note 57). When fused it forms a semi-transparent, yellow mass, and it is thus that it enters the market. The specific gravity of native orpiment is 3.4, and that of the artificially fused mass 2.7. It is used as a yellow pigment, and owing to its insolubility in water and acids it is less injurious than the other compounds corresponding to arsenious acid. To the type AsX_2 belongs realgar, AsS ; the molecule is probably As_4S_4 . **Realgar** (*sandaraca*) occurs native in brilliant red crystals of specific gravity 3.59, and may be prepared artificially by fusing together arsenic and sulphur in the proportions indicated by its formula. It is prepared in large quantities by distilling a mixture of sulphur and arsenical pyrites. Like orpiment it dissolves in calcium sulphide, and even in caustic potash. It is used for signal lights and fireworks, because it deflagrates and gives a large and very brilliant white flame with nitre.

With antimony, sulphur gives a tri- and a penta-sulphide. The former, Sb_2S_3 , which corresponds with antimonious oxide, occurs native (Chap. XIX.) in a crystalline form: its sp. gr. is then 4.9, and it forms brilliant rhombic crystals of a grey colour, which fuse when heated. A substance of the same composition is obtained as an amorphous orange powder by passing sulphuretted hydrogen into an acid solution of antimonious oxide. In this respect antimonious oxide again reacts like arsenious acid, and the sulphides of both are soluble in ammonium and potassium sulphides, and, especially in the case of arsenious sulphide, are easily obtained in colloidal solutions. By prolonged boiling with water, antimonious sulphide may be entirely converted into the oxide, hydrogen sulphide being evolved (Elbers). Native antimony sulphide, or the orange precipitated trisulphide when fused with dry, or boiled with dissolved, alkalis, forms a dark-coloured mass (Kermes mineral) formerly much used in medicine, which contains a mixture of antimonious sulphide and oxide. There are also compounds of these substances. A so-called antimony vermilion is much used as a dye; it is prepared by boiling sodium thiosulphate (six parts) with antimony trichloride (five parts) and water (fifty parts). This substance probably contains an oxysulphide of antimony—that is, a portion of the oxygen in the oxide of antimony in it is replaced by sulphur. Red antimony ore, and antimony glass, which is obtained by fusing the trisulphide with antimonious oxide, have a similar composition, Sb_2OS_2 . In the arts, the **antimony pentasulphide**, Sb_2S_5 , is the most frequently used of the sulphur compounds of antimony. It is formed by the action of acids on the so-called Schlippe's salt, which is a **sodium thio-ortho-antimonate**, $\text{SbS}(\text{NaS})_3$, corresponding with (Chap. XIX., note 41a) ortho-antimonic acid, $\text{SbO}(\text{OH})_3$, with the replacement of oxygen by sulphur. It is obtained by boiling finely powdered native antimony trisulphide with twice its weight of sodium carbonate, and half its weight of sulphur and of lime, in the presence of a considerable quantity of water. The processes taking place are as follows:—The sodium carbonate is converted into hydroxide by the lime, and then forms sodium sulphide with the sulphur; the sodium sulphide then dissolves the antimony sulphide, which in this form already combines with the greatest amount of sulphur, so that a compound is formed corresponding with antimony pentasulphide dissolved in sodium sulphide. The solution is filtered and crystallised, care being taken to prevent access of air, which oxidises the sodium sulphide. This salt crystallises in large, yellowish crystals, which are easily soluble in water and have the composition $\text{Na}_4\text{SbS}_5 \cdot 9\text{H}_2\text{O}$. When heated they lose their water of crystallisation and then fuse without alteration, but when in solution, and even in the crystalline form,

Turning to the oxygen compounds of sulphur, mention must first be made of the fact that the acids derived from chlorine, phosphorus, and carbon are the oxidised hydrogen compounds of these elements, and therefore we can form an idea of the acid hydrates of sulphur, or of the **normal acids of sulphur**, by representing them as the oxidised products of sulphuretted hydrogen—

HCl	H ₂ S	H ₃ P	H ₄ C
HClO	H ₂ SO(?)	H ₃ PO(?)	H ₄ CO
HClO ₂	H ₂ SO ₂ (?)	H ₃ PO ₂	H ₄ CO ₂
HClO ₃	H ₂ SO ₃	H ₃ PO ₃	H ₄ CO ₃
HClO ₄	H ₂ SO ₄	H ₃ PO ₄	H ₄ CO ₄ ³⁰

this salt turns brown in air, owing to the oxidation of the sulphur and the breaking up of the compound. As it is used in medicine, especially in the preparation of antimony pentasulphide, it is kept under a layer of alcohol, in which it is insoluble. Acids precipitate antimony pentasulphide from a solution of this salt, as an orange powder, insoluble in acids and very frequently used in medicine (*sulfur auratum antimonii*). This substance when heated evolves vapours of sulphur, and leaves antimony trisulphide behind.

Mercury forms with sulphur, compounds of the same types as those formed with oxygen. Mercurous sulphide, Hg₂S, readily splits up into mercury and mercuric sulphide. It is obtained by the action of sulphuretted hydrogen on solutions of salts of the type HgX. Mercuric sulphide, HgS, corresponding with the oxide, is **cinnabar**; it is obtained as a black precipitate by the action of an excess of sulphuretted hydrogen on solutions of mercuric salts. It is insoluble in acids, and is therefore precipitated in their presence. If a certain amount of water containing sulphuretted hydrogen is added to a solution of mercuric chloride, it first gives a white precipitate of the composition Hg₃S₂Cl₂—that is, a compound HgCl₂·2HgS, a sulphoehloride of mercury similar to the oxychloride. But in the presence of an excess of sulphuretted hydrogen, the black precipitate of mercuric sulphide is formed. In this state it is not crystalline (the red variety is formed by the prolonged action of polysulphides of ammonium upon the black HgS), but if it is heated to its temperature of volatilisation it forms a red crystalline sublimate which is identical with native cinnabar. In this form its specific gravity is 8·0, and it forms a red powder, owing to which it is used as a red pigment (vermilion) in oil, pastel, and other paints. It is so little attacked by reagents that even nitric acid has no action on it, and the gastric juices do not dissolve it, so that it is not poisonous. When heated in air, the sulphur burns away and leaves metallic mercury. On a large scale, cinnabar is usually prepared in the following manner: 300 parts of mercury and 115 parts of sulphur are mixed together as intimately as possible and poured into a solution of 75 parts of caustic potash in 425 parts of water, and the mixture is heated at 50° for several hours. Red mercury sulphide is thus formed, and separates out from the solution. The reaction which takes place is as follows: A soluble compound, K₂HgS₂, is first formed; this compound is able to separate in colourless silky needles, which are soluble in the caustic potash, but are decomposed by water, and at 50°; this solution (perhaps by attracting oxygen from the air) slowly deposits HgS in a crystalline form.

It is worthy of remark that Linder and Picton obtained complex compounds of many of the sulphides of the heavy metals (Ca, Hg, Sb, Zn, Cd, Ag, Au) with H₂S; for example, H₂S₇CuS (by the action of H₂S upon the hydrate of oxide of copper), H₂S₉CuS (in the presence of acetic acid and with an excess of H₂S), &c.

³⁰ There are four typical hydrogen compounds, RH, RH₂, RH₃, and RH₄, and each of them has its typical oxide. Beyond H₄ and O₄ combination does not proceed (Chap. XV.).

In the case of chlorine, if not all the hydrates, at all events, salts of all the normal hydrates are known, whilst in the case of sulphur only the acids H_2S , H_2SO_3 , and H_2SO_4 are known. But, on the other hand, the latter are obtained not only as hydrates, but also as stable anhydrides, SO_2 and SO_3 , which are formed with the evolution of heat from sulphur and oxygen; 32 parts of sulphur in combining with 32 parts of oxygen—that is, in forming SO_2 —evolve 71,000 heat units,³¹ and if the oxidation proceeds to the formation of SO_3 , 103,000 heat units are evolved. These figures may be compared with those which correspond with the passage of carbon into CO and CO_2 , when 29,000 and 97,000 units of heat are evolved. This determines the stability of the higher oxides of sulphur, and also expresses the peculiarity of sulphur as an element which, although an analogue of oxygen, forms stable compounds with it, and thus fundamentally differs from chlorine. The higher and lower oxides of chlorine are powerful oxidising agents, whilst the higher oxide of sulphur, SO_3 , has but feeble oxidising powers, and the lower oxide, SO_2 , frequently acts as a reducing agent, and is formed by the direct combustion of sulphur, just as carbonic anhydride, CO_2 , proceeds from the combustion of carbon. In the combustion of sulphur, and also in the oxidation (roasting) of the sulphides and polysulphides by their ignition in air, sulphurous oxide, or **sulphurous anhydride** or **sulphur dioxide**, SO_2 ,^{31a} is exclusively formed. It is prepared on a large scale, by burning sulphur or roasting iron pyrites or other sulphides,³² for the manufacture of sulphuric acid (Chap. VI.), and for direct application in the manufacture of wine, for bleaching tissues and for other purposes. In the latter instances its application is based on the fact that sulphurous anhydride acts on certain vegetable matters, and has the property of a reducing and feeble acid.^{32a}

³¹ Rhombic sulphur, 71,080 heat units; monoclinic sulphur, 71,720 units, according to Thomsen.

^{31a} However, when sulphur or metallic sulphides burn in an excess of air, there is always formed a certain, although small, amount of SO_3 , which gives sulphuric acid with the moisture of the air.

³² The enormous amount of sulphuric acid now manufactured is chiefly prepared by roasting native pyrites, but a considerable amount of the SO_2 used for this purpose is obtained by roasting zinc blende (ZnS) and copper and lead sulphides. A certain amount is also procured from soda refuse (note 6) and from the residues obtained from the purification of coal gas.

^{32a} Sulphurous anhydride is also obtained by the decomposition of many sulphates, especially of the heavy metals, by the action of heat; but this requires a very powerful heat. This formation of sulphurous anhydride from sulphates is based on the decomposition proper to sulphuric acid itself. When sulphuric acid is strongly heated (for instance, by dropping it upon an incandescent surface) it is decomposed into water, oxygen, and sulphurous anhydride—that is, into those compounds from which it is

In the laboratory—that is, on a small scale—sulphurous anhydride is best prepared by deoxidising sulphuric acid by heating it with charcoal, or with copper, sulphur, mercury, &c. Charcoal produces this decomposition of sulphuric acid at but moderately high temperatures; it is itself converted into carbonic anhydride,^{32b} so that when sulphuric acid is heated with charcoal it evolves a mixture of sulphurous and carbonic anhydrides: $C + 2H_2SO_4 = CO_2 + 2SO_2 + 2H_2O$. The metals which are unable to decompose water, and which do not, therefore, expel hydrogen from sulphuric acid, are frequently capable of decomposing sulphuric acid, with the evolution of sulphurous anhydride, just as they decompose nitric acid, forming the lower oxides of nitrogen. These metals are silver, mercury, copper, lead, and others. Thus, for example, the action of copper on sulphuric acid may be expressed by the following equation: $Cu + 2H_2SO_4 = CuSO_4 + SO_2 + 2H_2O$. In the laboratory this reaction is carried on in a flask with a gas-conducting tube, and does not take place unless aided by heat.³³

In its physical and chemical properties sulphurous anhydride presents a great **resemblance to carbonic anhydride**. It is a heavy gas, somewhat considerably soluble in water, very easily condensed into a liquid; it forms normal and acid salts, does not evolve oxygen under the direct action of heat,³⁴ although such metals as sodium and magnesium burn in it, just as in carbonic anhydride. It has a suffocating odour, which is well known owing to its being evolved when sulphur or sulphur matches are burnt. In characterising the properties of sulphurous anhydride, it is very important to remember (Chap. II.) also that it is more easily liquefied (at -10° , or at 0° under two atmospheres pressure) than carbonic anhydride (thirty-six atmospheres

formed. A similar decomposition proceeds during the ignition of many sulphates. Even so stable a sulphate as gypsum does not resist the action of very high temperatures, but is decomposed in the same manner, lime being left behind. The decomposition of sulphates by heat is accomplished with still greater facility in the presence of sulphur, because in this case the liberated oxygen combines with the sulphur and the metal is able to form a sulphide. Thus when ferrous sulphate (green vitriol) is ignited with sulphur, it gives ferrous sulphide and sulphurous anhydride: $FeSO_4 + 2S = FeS + 2SO_2$. At 400° sulphuric acid and sulphur give an extremely uniform stream of pure sulphurous anhydride, so that it is best prepared on a manufacturing scale by this method. Iron pyrites, FeS_2 , when heated to 150° with sulphuric acid (sp. gr. 1.75) in cast-iron vessels, also gives an abundant and uniform supply of sulphurous anhydride.

^{32b} Mellitic acid is formed at the same time (Verneuille).

³³ The thermochemical data connected with this reaction are as follows: A molecule of hydrogen, H_2 , in combining with oxygen ($O = 16$), develops about 69,000 heat units—whilst the molecule of SO_2 in combining with oxygen only develops about 32,000 heat units—that is, about half as much—and therefore those metals which cannot decompose water may still be able to deoxidise sulphuric into sulphurous acid.

³⁴ That is, it only dissociates and re-forms the original product on cooling.

at 0°),³⁵ that it is more soluble than carbonic anhydride (Vol. I., p. 79) : at 0° , 100 vols. of water dissolve 180 vols. of carbonic anhydride and 688 vols. of sulphuric anhydride ; that the molecular weight of SO_2 is 64, and that of CO_2 , 44, and that the density of liquid sulphurous anhydride at 0° is 1.43 (molecular volume=45) and that of carbonic anhydride, 0.95 (molecular volume=49). Although sulphur dioxide is the anhydride of an acid, nevertheless, like carbonic anhydride, it does not form any stable compounds with water, but gives a solution from which it may be entirely expelled by the action of heat.³⁶ The acid character of sulphurous anhydride is clearly expressed by the fact that it is entirely absorbed by alkalis, with which it forms acid and normal salts readily soluble in water. With salts of barium, calcium, and the heavy metals, the normal salts of the alkalis, M_2SO_3 , give precipitates exactly like those formed by the carbonates. In general, the salts of sulphurous acid are closely analogous to the corresponding carbonates.

One of the most widely used salts, **acid sodium sulphite**, NaHSO_3 , may be obtained by passing sulphurous anhydride into a solution of sodium hydroxide. It is also formed by saturating a solution of sodium carbonate with the gas (carbonic anhydride is then given off), and as the solubility of the acid sulphite is much greater than that of the carbonate, a further quantity of the latter may be dissolved after the passage of the sulphurous anhydride, so that in this manner a very strong solution of the sulphite may be ultimately formed, from which it may be obtained in a crystalline form, either by cooling and evaporating (without heating, for then the salt would give off sulphurous anhydride) or by adding alcohol to the solution. When exposed to the air this salt loses sulphurous anhydride and attracts oxygen, which converts it into sodium sulphate. The acid sulphites of the alkali metals are able to combine not only with oxygen, but also with many other substances—for example, a solution of the sodium salt dissolves sulphur, forming sodium thiosulphate, gives crystalline compounds with the aldehydes and ketones, and dissolves many bases, converting them into double sulphites. Having the power of attracting or

³⁵ At a given temperature the pressure of this gas evolved from any salt will be less than that of carbonic anhydride, if we compare the separation of a gas from its salts with the phenomenon of evaporation, as was done in discussing the decomposition of calcium carbonate.

Liquid sulphurous anhydride is used on a large scale (Pictet) for the production of cold.

³⁶ De la Rive, Pierre, and more especially Roozeboom, have investigated the crystallo-hydrate which is formed by sulphurous anhydride and water at temperatures below 7° under the ordinary pressure, and in closed vessels (at temperatures below 12°). Its composition is $\text{SO}_2 \cdot 7\text{H}_2\text{O}$, and its density 1.2. This hydrate corresponds with the similar hydrate $\text{CO}_2 \cdot 8\text{H}_2\text{O}$ obtained by Wroblewsky.

absorbing oxygen, acid sodium sulphite is also able to absorb chlorine, and is therefore employed, like sodium thiosulphate, for the removal of chlorine (as an antichlor), especially in the bleaching of fabrics, when it is necessary to remove the last traces of the chlorine held in the tissues, which might otherwise have an injurious effect on them. If a solution of an alkali hydroxide is divided into two parts, and one half is saturated with sulphurous anhydride, and the other half then added to it, a normal salt will be obtained in the solution, having an alkaline reaction, like a solution of sodium carbonate. The acid salt has a neutral reaction.^{36a} Like sodium carbonate, **normal sodium sulphite** has the composition $\text{Na}_2\text{SO}_3 \cdot 10\text{H}_2\text{O}$, and its maximum solubility is at 33° —in a word, it very closely resembles sodium carbonate. Although this salt does not give off sulphurous anhydride from its solution, it is able, like the acid salt, to absorb oxygen from the air, and is then converted into sodium sulphate.³⁷

Besides the acid character we must also point out the reducing character of sulphurous anhydride. The **reducing action** of sulphurous acid, its anhydride and salts, is due to their property of passing into sulphuric acid and sulphates. The reducing action of the sulphites is particularly energetic, so that they even convert nitric oxide into nitrous oxide: $\text{K}_2\text{SO}_3 + 2\text{NO} = \text{K}_2\text{SO}_4 + \text{N}_2\text{O}$. The salts of many of the higher oxides are converted into those of the lower—for example, FeX_3 into FeX_2 , CuX_2 into CuX , HgX_2 into HgX ; thus, $2\text{FeX}_3 + \text{SO}_2 + 2\text{H}_2\text{O} = 2\text{FeX}_2 + \text{H}_2\text{SO}_4 + 2\text{HX}$. In the presence of water, sulphurous anhydride is oxidised by chlorine ($\text{SO}_2 + 2\text{H}_2\text{O} + \text{Cl}_2 = \text{H}_2\text{SO}_4 + 2\text{HCl}$),

^{36a} Schwicker (1889), by saturating NaHSO_3 with potash, or KHSO_3 with soda, obtained NaKSO_3 (in general sulphurous acid easily forms double salts), in the first instance with H_2O , and in the second instance with $2\text{H}_2\text{O}$. This is probably owing to the different media in which the crystals are formed, but is not infrequently regarded as due to the different characters of the two hydrogens of sulphurous acid, which is admissible if sulphurous and sulphuric acids are composed of one and the same residue, 'sulphoxyl,' (see further on) HSO_3 , combined with H or HO. And if sulphurous acid is $\text{H}(\text{SO}_3\text{H})$, that is, $\text{HSO}_2(\text{OH})$, the two hydrogens in its molecule would be of different character, one being directly combined with S, and the other through the medium of oxygen in the form OH. In this case one of the above salts will be KSO_3ONa and the other NaSO_3OK ; that is to say, they are isomeric. It cannot be denied that this view is highly probable, especially as it simplifies the explanation of certain reactions of sulphurous acids, but still, in my opinion, there can be no certainty of this being the case, for there exists a chloranhydride, SOCl_2 , which is equivalent to sulphurous acid, $\text{SO}(\text{OH})_2$, with the substitution of OH by chlorine, and yet nothing indicates the possibility of two isomeric chloranhydrides, ClSO_2OH and HSO_2OCl . For my part, I consider that the isomerism of the above two salts cannot be considered as proved, and that it is therefore impossible to be quite certain of it.

³⁷ The normal salts of calcium and magnesium are slightly, and the acid salts freely, soluble in water. These acid sulphites are much used in practice; thus, calcium bisulphite is employed in the manufacture from sawdust of cellulose, which is largely made use of for mixing with fibrous matter in the manufacture of paper.

iodine, nitrous acid, hydrogen peroxide, hypochlorous acid, chloric acid, and other oxygen compounds of the halogens, chromic, manganic, and many other metallic acids and higher oxides, as well as all peroxides. Free oxygen in the presence of spongy platinum is able to oxidise sulphurous anhydride even in the absence of water, in which case sulphuric anhydride, SO_3 , is formed, so that the latter may be prepared by passing a mixture of sulphurous anhydride and oxygen over incandescent spongy platinum, or, as it is prepared on a large scale in chemical works (Winkler's process), by passing this mixture over asbestos or pumice-stone moistened with a solution of a platinum salt and ignited. Sulphurous anhydride is completely absorbed by certain higher oxides—for instance, by barium peroxide and lead dioxide ($\text{PbO}_2 + \text{SO}_2 = \text{PbSO}_4$).³⁸

There are, however, cases where sulphurous anhydride acts as an oxidising agent—that is, it is **deoxidised** in the presence of substances which are capable of absorbing oxygen with still greater energy than the sulphurous anhydride itself. This oxidising action proceeds with the formation of sulphuretted hydrogen or of sulphides, while the reducing agent is oxidised at the expense of the oxygen of the sulphurous anhydride. Thus stannous chloride, SnCl_2 , in an aqueous solution gives a precipitate of stannic sulphide, SnS_2 , with sulphurous anhydride—that is, the latter is deoxidised to sulphuretted hydrogen, while SnX_2 is oxidised into SnX_4 . A solution of sulphurous anhydride, in acting on zinc, which passes into solution, does not evolve hydrogen, but combines directly,³⁹ forming a salt of **hydrosulphurous**

³⁸ This reaction is taken advantage of for removing sulphurous anhydride from a mixture of gases. Lead dioxide, PbO_2 , is brown, and when combined with sulphurous anhydride it forms lead sulphate, PbSO_4 , which is white, so that the reaction is evident from both the change in colour and the development of heat. Sulphurous anhydride is slowly decomposed by the action of light, with the separation of sulphur and formation of sulphuric anhydride. This explains the fact that sulphurous anhydride prepared in the dark gives a white precipitate of silver sulphite, Ag_2SO_3 , with silver perchlorate, AgClO_4 , but when prepared in the light, even in diffused light, it gives a dark precipitate. This naturally depends on the fact that the sulphur liberated then forms silver sulphide, which is black. It is notable that SO_2 combines directly with some salts, for instance, KI (Peshar, 1900), KCNS (Fox, 1902), &c.

³⁹ Schönbein observed that the liquid turns yellow, and acquires the faculty of **decolorising** litmus and indigo. Schützenberger showed that this depends on the formation of a zinc salt of a peculiar and very powerfully reducing acid, for with cupric salts the yellow solution gives a red precipitate of cuprous hydride or metallic copper, and it completely reduces salts of silver and mercury. An exactly similar solution is obtained by the action of zinc on sodium bisulphite without access of air and in the cold. The yellow liquid absorbs oxygen from the air with great avidity, and forms a sulphate. If a solution of NaHSO_3 be treated with zinc dust in the presence of an excess of SO_2 $2\text{NaHSO}_3 + \text{Zn} + \text{SO}_2 = \text{ZnSO}_3 + \text{Na}_2\text{S}_2\text{O}_4 + \text{H}_2\text{O}$ and be then precipitated with lime, the filtrate will contain the sodium salt. With NaCl strong solutions deposit crystals, which should be kept and dried without access of air. The solution of these crystals has the

acid, ZnS_2O_4 . The free acid is still less stable than the salt ($\text{H}_2\text{S}_2\text{O}_4 = \text{H}_2 + 2\text{SO}_2$).

The faculty of sulphurous anhydride of combining with various substances is evident from its compounds with hydrogen and with oxygen, and also appears in the fact that, like carbonic oxide, it combines with chlorine, forming a chloranhydride of sulphuric acid, SO_2Cl_2 , to which we shall afterwards return. The same faculty for combination also appears in the exceedingly characteristic formation of a peculiar series of salts obtained by Pelouze and Frémy. At a temperature of -10° or below, nitric oxide, NO , is absorbed by alkaline solutions of the alkali sulphites, forming a peculiar series of **nitrosulphates**. At a higher temperature these salts are not formed, but the nitric oxide is reduced to nitrous oxide. But in the cold, and after a certain time, the liquid saturated with nitric oxide gives prismatic crystals resembling those of nitre. The composition of the potassium salt is $\text{K}_2\text{SN}_2\text{O}_5$ —that is, the salt contains the elements of potassium sulphite and of nitric oxide.⁴⁰

above-mentioned decolorising and reducing properties. These crystals contain a sodium salt of a lower acid which is called *hydrosulphurous acid* ($= \text{H}_2 + 2\text{SO}_2$); their composition was at first supposed to be HNaSO_2 , but it was afterwards proved that they do not contain hydrogen, and present the composition $\text{Na}_2\text{S}_2\text{O}_4 + 2\text{H}_2\text{O}$ (Berthsen). The same salt is formed by the action of a galvanic current on a solution of sodium bisulphite, owing to the action of the hydrogen at the moment of its liberation. If SO_2 resembles CO_2 in its composition, then hyposulphurous acid, $\text{H}_2\text{S}_2\text{O}_4$, resembles oxalic acid, $\text{H}_2\text{C}_2\text{O}_4$. Perhaps an analogue of formic acid, SH_2O_2 , will be discovered. Moissan (1902) showed that potassium hydride and also the hydrides of Na, Li, Sr, &c., directly absorb SO_2 if it is in a state of dilution or rarefaction (otherwise an explosion will ensue), forming salts of hydrosulphurous acid with the evolution of hydrogen, $2\text{KH} + 2\text{SO}_2 = \text{K}_2\text{S}_2\text{O}_4 + \text{H}_2$.

⁴⁰ The instability of this salt is very great, and may be compared with that of the compound of ferrous sulphate with nitric oxide, for when heated under the contact influence of spongy platinum, charcoal, &c., it splits up into potassium sulphate and nitrous oxide. At 130° the dry salt gives off nitric oxide, and re-forms potassium sulphite. The free acid has not yet been obtained. These salts resemble the **sulphonitrites** discovered by Frémy in 1845. They are obtained by passing sulphurous anhydride through a concentrated and strongly alkaline aqueous solution of potassium nitrite. They are soluble in water, but are precipitated by excess of alkali. The first product of the action has the composition $\text{K}_3\text{NS}_3\text{O}_9$. It is then converted by the further action of sulphurous anhydride, water, and other reagents into a series of similar complex salts, many of which give well-formed crystals. One must suppose that the chief cause of the formation of these very complex compounds is that they contain unsaturated compounds, NO , KNO_2 , and KHSO_3 , all of which are subject to oxidation and further combination, and therefore easily combine among each other. The decomposition of these compounds, when their solutions are heated, is due to the fact that the decoxidant, sulphurous anhydride, reduces the nitrous acid, $\text{NO}(\text{OH})$, to ammonia. In my opinion the composition of the sulphonitrites may be very simply referred to the composition of ammonia, in which the hydrogen is replaced by the radicle of the sulphates. If we represent the composition of potassium sulphate as $\text{KO} \cdot \text{KSO}_3$, the group KSO_3 will be equivalent (according to the law of substitution) to HO and to hydrogen. With hydrogen, it forms acid potassium sulphite, KHSO_3 . Hence the group KSO_3 may also replace the hydrogen in ammonia. Judging by my analysis (1870), the extreme limit of this substitution,

There are also several other substances, formed by the oxides of nitrogen and sulphur, which belong to this class of complex and, under some circumstances, unstable compounds. In the manufacture of sulphuric acid, both these classes of oxides come into contact with each other in the lead chambers, and if there be insufficient water for the formation of sulphuric acid they give crystalline compounds, termed **chamber crystals**. As a rule, the composition of the crystals is expressed by the formula NHSO_5 . This is a compound of the radicles NO_2 , of nitric acid, and HSO_3 , of sulphuric acid, or **nitrosulphuric acid**, $\text{NO}_2 \cdot \text{SHO}_3$, if sulphuric acid be expressed as $\text{OH} \cdot \text{SHO}_3$ and nitric acid by $\text{NO}_2 \cdot \text{OH}$. This substance is best understood as sulphurous acid, SH_2O_3 , in which one hydrogen is replaced by the residue of nitric acid, $\text{NO}_2 : \text{S}(\text{NO}_2)\text{HO}_3$. The tabular crystals of this substance fuse at about 70° , and are formed by the direct action of both nitrous anhydride and nitric peroxide (but not NO , which is not absorbed by sulphuric acid) on sulphuric acid (Weltzien and others), and especially on sulphuric acid containing an anhydride and the lower oxides of sulphur and nitric acid.⁴¹

$\text{N}(\text{HSO}_3)_3$, agrees with that of the sulphonitrite, which is easily formed, simultaneously with alkali, by the action of potassium sulphite on potassium nitrite, according to the equation: $3\text{K}(\text{KSO}_3) + \text{KNO}_2 + 2\text{H}_2\text{O} = \text{N}(\text{KSO}_3)_3 + 4\text{HKO}$. The researches of Berglund, and especially of Raschig (1887), fully verified my conclusions, and showed that we must distinguish the following types of salts, corresponding with ammonia, where X stands for the sulphonic group, HSO_3 , in which the hydrogen is replaced by potassium and is hence KSO_3 : (1) NH_2X , (2) NHX_2 , (3) NH_3 , (4) $\text{N}(\text{OH})\text{XH}$, (5) $\text{N}(\text{OH})\text{X}_2$, (6) $\text{N}(\text{OH})_2\text{X}$, just as $\text{NH}_2(\text{OH})$ is hydroxylamine, $\text{NH}(\text{OH})_2$, the hydrate of nitrous oxide, and $\text{N}(\text{OH})_3$, orthonitrous acid, as follows from the law of substitution. This class of compounds is in most intimate relation with the amides of sulphuric acid and with the series of sulphonitrous compounds, corresponding with 'chamber crystals' and their acids, which we shall consider later. The researches of Divers and his assistants explained the relations of the substances formed to the ammonia derivatives. As an instance, we may mention that when a solution of 2HNaSO_3 with NaNO_2 is cooled to 0° it gives NaHO and a salt, $\text{N}(\text{OH})(\text{NaSO}_3)_2$, which is very soluble, and gives a less soluble salt with KCl . On boiling, a solution of this salt first gives $\text{KHSO}_4 + \text{N}(\text{OH})(\text{KSO}_3)$ and then the whole of the potassium is converted into sulphate: $\text{N}(\text{OH})(\text{KSO}_3)_2 + 2\text{H}_2\text{O} = \text{K}_2\text{SO}_4 + \text{NH}_2(\text{OH})\text{H}_2\text{SO}_4$ (sulphate of hydroxylamine). With sulphurous oxide, a strong solution of hydrochloride of hydroxylamine forms directly a crystalline, slightly soluble mono-substituted acid, $\text{NH}_2\text{SO}_3\text{H} = \text{NH}_2\text{OH} + \text{SO}_2$. With water the di- and tri-substituted acids NHX_2 and NX_3 readily form H_2SO_4 and the mono-substituted acid. The di-substituted acid, NHX_2 , is easily formed by the action of NH_3 on the first chloranhydride of sulphuric acid, SO_3HCl . Compounds containing hydroxyl, for instance, $\text{N}(\text{OH})\text{X}_2$ are, as a rule, formed by the action of nitric acid, which, in the aspect of an ortho-hydrate, is equivalent to $\text{N}(\text{OH})_3$.

⁴¹ Nitroso-sulphuric acid, NHSO_5 , readily crystallises, melts at 73° , gives a chloranhydride and anhydride (see later); but it does not form any salts, because it is decomposed by water and still more easily by alkalies. In the sulphuric acid chambers the lower oxides of nitrogen and sulphur take part in the reaction. They are oxidised by the oxygen of the air, and form nitro-sulphuric acid—for example, $2\text{SO}_2 + \text{N}_2\text{O}_5 + \text{O}_2 + \text{H}_2\text{O} = 2\text{NHSO}_5$. This compound dissolves in strong sulphuric acid without changing, and

Thiosulphuric acid, $\text{H}_2\text{S}_2\text{O}_3$ —that is, a compound of sulphurous acid and sulphur—also belongs to the products of combination of sulphurous acid. In the same way that sulphurous acid, H_2SO_3 , gives H_2SO_4 with oxygen, so it gives $\text{H}_2\text{S}_2\text{O}_3$ with sulphur. In a free state it is very unstable, and it is only known in the form of its salts, which proceed from the direct action of sulphur on the normal sulphites; if endeavours are made to separate it in a free state, it immediately splits up into those elements from which it might be formed—that is, into sulphur and sulphurous acid. The most important of its salts is **sodium thiosulphate** (known as hyposulphite), $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, which occurs in colourless crystals, and is unacted on by atmospheric oxygen either when in a dry state or in solution. Many other salts of this acid are easily formed by means of this one,^{11a} although this cannot be done with all bases, for such of the latter as alumina, ferric oxide, chromium oxide, and others do not give compounds with thiosulphuric acid, just as they do not form stable compounds with carbonic acid. Whenever these salts might be formed, they (like the acid) split up into sulphurous acid and sulphur, and furthermore the elements of thiosulphuric acid in many cases act in a reducing manner, forming sulphuric acid and taking up the oxygen from reducible oxides. Thus, when treated with a thiosulphate the soluble ferric salts give a precipitate of sulphur and form ferrous salts. The thiosulphates of the metals of the alkalis are obtained directly by boiling a solution of their sulphites with sulphur: $\text{Na}_2\text{SO}_3 + \text{S} = \text{Na}_2\text{S}_2\text{O}_3$. The same salts are formed by the action of sulphurous anhydride on solutions of the sulphides; thus, sodium sulphide dissolved in water gives sulphur and sodium thiosulphate

when such a solution is diluted (when the sp. gr. falls to 1·5), it splits up into sulphuric acid and nitrous anhydride, and by the action of sulphurous anhydride is converted into nitric oxide, which by itself (in the absence of nitric acid or oxygen) is insoluble in sulphuric acid. These reactions are taken advantage of in retaining the oxides of nitrogen in the Gay-Lussac coke-towers, and for extracting the absorbed oxides of nitrogen from the resultant solution in the Glover tower. Although nitric oxide is not absorbed by sulphuric acid, it reacts (Rose, Brüning) on its anhydride, and forms sulphurous anhydride and a crystalline substance, $\text{N}_2\text{S}_2\text{O}_5 = 2\text{NO} + 3\text{SO}_3 - \text{SO}_2 = \text{N}_2\text{O}_3 \cdot 2\text{SO}_3$. This may be regarded as the anhydride of nitro-sulphuric acid, because $\text{N}_2\text{S}_2\text{O}_5 = 2\text{NHSO}_3 - \text{H}_2\text{O}$; it melts at 217° , and, like nitro-sulphuric acid, is decomposed by water into nitro-sulphuric acid and nitrous anhydride. Since boric and arsenious anhydrides, alumina, and other oxides of the form R_2O_3 are able to combine with sulphuric anhydride to form similar compounds decomposable by water, the above compound does not present any exceptional phenomenon. Sulphuric anhydride also combines with NO_2 , forming $\text{N}_2\text{O}_5 \cdot 2\text{SO}_3$, which under the action of heat evolves oxygen and gives the above anhydride, $\text{N}_2\text{S}_2\text{O}_5$. The substance, $\text{NOCl} \cdot \text{SO}_3$, obtained by Weber by the action of nitrosyl chloride upon sulphuric anhydride belongs to this class of compounds. But with H_2SO_4 the nitrosyl chloride gives also NHSO_3 , with the evolution of HCl .

^{11a} Many double salts of thiosulphuric acid are known; for instance, $\text{PbS}_2\text{O}_3 \cdot 3\text{Na}_2\text{S}_2\text{O}_3 \cdot 12\text{H}_2\text{O}$; $\text{CaS}_2\text{O}_3 \cdot 3\text{K}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, &c. (Portman, Schwicker, Fock, and others).

when a stream of sulphurous anhydride is passed through it: $2\text{Na}_2\text{S} + 3\text{SO}_2 = 2\text{Na}_2\text{S}_2\text{O}_3 + \text{S}$. The polysulphides of the alkali metals, when left exposed to the air, attract oxygen and also form thiosulphates.⁴² A mixture of solutions of Na_2S and Na_2SO_4 gives 2NaI and $\text{Na}_2\text{S}_2\text{O}_3$ under the action of iodine.

⁴² Thus, when alkali waste, which contains calcium sulphide, undergoes oxidation in the air, it forms first a calcium polysulphide, and then calcium thiosulphate, CaS_2O_3 . When iron or zinc acts on a solution of sulphurous acid, besides the hyposulphurous acid first formed, a mixture of sulphite and thiosulphate is obtained (note 39), $3\text{SO}_2 + \text{Zn} = \text{ZnSO}_3 + \text{ZnS}_2\text{O}_3$. In this case, as in the formation of hyposulphurous acid, there is no hydrogen liberated. One of the most common methods for preparing thiosulphates consists in the **action of sulphur on the alkalis**. The reaction is accomplished by the formation of sulphides and thiosulphates, just as the reaction of chlorine on alkalis is accompanied by the formation of hypochlorites and chlorides; hence, in this respect, the thiosulphates hold the same position in the order of the compounds of sulphur as the hypochlorites do among the chlorine compounds. The reaction of caustic soda on an excess of sulphur may be expressed thus: $6\text{NaHO} + 12\text{S} = 2\text{Na}_2\text{S}_5 + \text{Na}_2\text{S}_2\text{O}_3 + 3\text{H}_2\text{O}$. Thus sulphur is soluble in alkalis. On a large scale sodium thiosulphate, $\text{Na}_2\text{S}_2\text{O}_3$, is prepared by first heating sodium sulphate with charcoal, to form sodium sulphide, which is then dissolved in water and treated with sulphurous anhydride. The reaction is complete when the solution has become slightly acid. A certain amount of caustic alkali is added to the slightly acid solution; a portion of the sulphur is thus precipitated, and the solution is then boiled and evaporated, when the salt crystallises out. Sodium thiosulphate is also prepared by the double decomposition of the soluble calcium thiosulphate with sodium sulphate or carbonate, in which case calcium sulphate or carbonate is precipitated. The calcium thiosulphate is prepared by the action of sulphurous anhydride on either calcium sulphide or alkali waste.

The crystals of sodium thiosulphate, $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, are stable, do not effloresce, and at 0° dissolve in one part of water, and at 20° in 0.6 part. The solution of this salt does not undergo any change when boiled for a short time, but after prolonged boiling it deposits sulphur. The crystals fuse at 56° , and lose all their water at 100° . When the dry salt is ignited it gives sodium sulphide and sulphate. With acids, a solution of the thiosulphate soon becomes cloudy and deposits an exceedingly fine powder of sulphur (note 10). If the amount of acid added is considerable, it also evolves sulphurous anhydride: $\text{H}_2\text{S}_2\text{O}_3 = \text{H}_2\text{O} + \text{S} + \text{SO}_2$. Sodium thiosulphate has many practical uses; it is used in photography for dissolving silver chloride and bromide. Its solvent action on silver chloride may be taken advantage of in extracting this metal as chloride from its ores. In dissolving, it forms a double salt of silver and sodium: $\text{AgCl} + \text{Na}_2\text{S}_2\text{O}_3 = \text{NaCl} + \text{AgNaS}_2\text{O}_3$. Sodium thiosulphate is an **antichlor**—that is, a substance which hinders the destructive action of free chlorine—owing to its being very easily oxidised by chlorine into sulphuric acid and sodium chloride. The reaction with iodine is different, and is remarkable for the accuracy with which it proceeds. The iodine takes up half the sodium from the salt and converts it into a tetrathionate, $2\text{Na}_2\text{S}_2\text{O}_3 + \text{I}_2 = 2\text{NaI} + \text{Na}_2\text{S}_4\text{O}_6$, and hence this reaction is employed for the determination of free iodine. As iodine is expelled from potassium iodide by chlorine, it is possible also to determine the amount of chlorine by this method if potassium iodide be added to a solution containing chlorine. And as many of the higher oxides are able to evolve iodine from potassium iodide, or chlorine from hydrochloric acid (for example, the higher oxides of manganese, chromium, &c.), it is also possible to determine the amounts of these higher oxides by means of sodium thiosulphate and liberated iodine. This forms the basis of the **iodometric methods** of volumetric analysis. The details of these methods will be found in works on analytical chemistry.

On adding a solution of a **lead salt** gradually to a solution of sodium thiosulphate, a white precipitate of lead thiosulphate, PbS_2O_3 , is formed (a soluble double salt is first

Although sulphur, oxidising at a high temperature, only forms a small quantity of sulphuric anhydride, SO_3 , and nearly all passes into sulphurous anhydride, still the latter may be converted into the higher oxide, or **sulphuric anhydride**, SO_3 , by many methods. Sulphuric anhydride is a solid crystalline substance at the ordinary temperature; it is easily fusible (15°) and volatile (46°), and rapidly attracts moisture. Although it is formed by the combination of sulphurous anhydride with oxygen, it is very prone to further combination, for instance, with water, hydrochloric acid, ammonia, many hydrocarbons, and even with sulphuric acid, boric and nitrous anhydrides, &c., and also with bases which burn directly in its vapour, forming sulphates in the presence of traces of moisture (see Chap. IX., note 29).^{12a} The oxidation of sulphurous anhydride, SO_2 , into sulphuric anhydride, SO_3 , is effected by passing a mixture of the former and dry oxygen or air over incandescent spongy platinum. An increase of pressure accelerates the reaction (Hänisch). If the product is passed into a cold vessel, crystalline sulphuric anhydride is deposited upon the sides of the vessel; but as it is difficult to avoid all traces of moisture it always contains compounds of its hydrates, $\text{H}_2\text{S}_2\text{O}_7$ and $\text{H}_2\text{S}_4\text{O}_{13}$, whose presence so modifies the properties of the anhydride (Weber) that formerly two modifications of the anhydride were recognised. The same sulphuric anhydride may be obtained from certain anhydrous or almost anhydrous, sulphates, which are decomposed by heat, whilst an impure but perfectly anhydrous anhydride is formed by distillation over phosphoric anhydride. For instance, acid sodium sulphate, NaHSO_4 , and the pyro- or di-sulphate, $\text{Na}_2\text{S}_2\text{O}_7$ (Chap. XII), formed from it, evolve sulphuric anhydride when ignited. Green vitriol—that is, ferrous sulphate, FeSO_4 —belongs to the number of those sulphates which easily give off sulphuric anhydride under the action of heat. It contains water of crystallisation and parts with it when heated, but the last equivalent of water is driven off with

formed, and if the action is rapid, lead sulphide). When this substance is heated at 200° , it undergoes a change and takes fire. In solution sodium thiosulphate rapidly reduces cupric salts to cuprous salts by means of the sulphurous acid contained in the thiosulphate, but the resultant cuprous oxide is not precipitated, because it passes into the state of a thiosulphate and forms a double salt. These double cuprous salts are excellent reducing agents. The solution, when heated, gives a black precipitate of copper sulphide.

At one time it was thought that all the salts of thiosulphuric acid only existed in combination with water, and it was then supposed that their composition was $\text{H}_4\text{S}_2\text{O}_6$, or H_2SO_2 , but Popp obtained the anhydrous salts.

^{12a} Liquid SO_3 dissolves flowers of sulphur and deposits a blue substance to which the composition S_2O_4 is ascribed, but which is not stable and readily decomposes into SO_2 and S (Weber, 1891). Nothing further is known about this substance. Selenium and tellurium give SSeO_3 and STeO_3 with SO_3 .

difficulty, just as is the case with magnesium sulphate, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$; however, when thoroughly heated, this evolution of sulphuric anhydride does take place, although not completely, because at a high temperature a portion of it is decomposed by the ferrous oxide ($\text{SO}_3 + 2\text{FeO}$), which is converted into ferric oxide, Fe_2O_3 , and in consequence part of the sulphuric anhydride is converted into sulphurous anhydride. Thus, the products of the decomposition of ferrous sulphate will be: ferric oxide, Fe_2O_3 , sulphurous anhydride, SO_2 , and sulphuric anhydride, SO_3 , according to the equation: $2\text{FeSO}_4 = \text{Fe}_2\text{O}_3 + \text{SO}_2 + \text{SO}_3$. As water still remains with the ferrous sulphate when it is heated, the result will partially consist of the hydrate H_2SO_4 , with anhydride, SO_3 , dissolved in it. Sulphuric acid was for a long time prepared in this manner; the process was formerly carried on on a large scale in the neighbourhood of Nordhausen, and hence the sulphuric acid prepared from ferrous sulphate is called **fuming** or **Nordhausen acid**. At the present time the fuming acid is prepared by passing the volatile products of the decomposition of ferrous sulphate through strong sulphuric acid prepared by the ordinary method. The sulphurous anhydride is insoluble in it, but it absorbs the sulphuric anhydride. Sulphuric anhydride may be prepared not only by igniting FeSO_4 or sodium pyrosulphate, $\text{Na}_2\text{S}_2\text{O}_7$ (the decomposition proceeds at 600°), but also by heating a mixture of the latter and MgSO_4 (Walters); in the former case a stable double salt, $\text{MgNa}_2(\text{SO}_4)_2$, finally remains. It is also obtained by the direct combination of SO_2 and O under the action of spongy platinum or asbestos coated with platinum black. Nordhausen sulphuric acid fumes in air, owing to its containing and easily giving off sulphuric anhydride, and it is therefore also called **fuming sulphuric acid**; these fumes are nothing but the vapour of sulphuric anhydride combining with the moisture in the air and forming non-volatile sulphuric acid (hydrate).⁴³

⁴³ Nordhausen sulphuric acid may serve as a very simple means for the preparation of sulphuric anhydride. For this purpose the Nordhausen acid is heated in a glass retort, whose neck is firmly fixed in the mouth of a well-cooled flask. The access of moisture is prevented by connecting the receiver with a drying-tube. On heating the retort, the vapours of sulphuric anhydride will pass over into the receiver, where they condense; the crystals of anhydride thus prepared will, however, contain traces of sulphuric acid—that is, of the hydrate. By repeatedly distilling over phosphoric anhydride, it is possible to obtain the pure anhydride, SO_3 , especially if the process be carried on without access of air in a closed vessel.

The ordinary sulphuric anhydride, which is imperfectly freed from the hydrate, is a snow-white, exceedingly volatile substance, which crystallises (generally by sublimation) in long silky prisms, and only gives the pure anhydride when carefully distilled over P_2O_5 . Freshly prepared crystals of almost pure anhydride fuse at 16° into a colourless liquid having a specific gravity 1.91 at 26° , and 1.81 at 47° ; it volatilises at 46° . After being kept for some time, the anhydride, even when containing only small traces of water,

Nordhausen sulphuric acid contains a peculiar compound of SO_3 and H_2SO_4 , or **pyrosulphuric acid**; an imperfect anhydride of sulphuric acid, $\text{H}_2\text{S}_2\text{O}_7$, analogous in composition with the salts $\text{Na}_2\text{S}_2\text{O}_7$, $\text{K}_2\text{Cr}_2\text{O}_7$, and bearing the same relation to H_2SO_4 that pyrophosphoric acid does to H_3PO_4 . The bond holding the sulphuric acid and anhydride together is unstable. This is obvious from the fact that the anhydride may easily be separated from this compound by the action of heat. In order to obtain the definite compound, the Nordhausen acid is cooled to 5° , or, better still, a portion of it is distilled until all the anhydride and a certain amount of sulphuric acid have passed over into the distillate, which will then solidify at the ordinary temperature, because the compound $\text{H}_2\text{SO}_4\cdot\text{SO}_3$ fuses at 35° . Although this substance reacts on water, bases, &c., like a mixture of $\text{SO}_3 + \text{H}_2\text{SO}_4$, still since a definite compound, $\text{H}_2\text{S}_2\text{O}_7$, exists in a free state and gives salts and a chloranhydride, $\text{S}_2\text{O}_5\text{Cl}_2$,⁴⁴ we must admit the existence of a definite pyrosulphuric acid, like pyrophosphoric acid, only that the latter has far greater stability and is not even converted into a perfect hydrate by water. Further, the salts $\text{M}_2\text{S}_2\text{O}_7$ dissolved in water react in the same manner as the acid salts MHSO_4 , whilst the imperfect

undergoes a change of the following nature: A small quantity of sulphuric acid combines by degrees with a large proportion of the anhydride, forming polysulphuric acids, $\text{H}_2\text{SO}_4\cdot n\text{SO}_3$, which fuse with difficulty (even at 100° , Marignae), but decompose when heated. In the entire absence of water this rise in the fusing-point does not occur (Weber), and then the anhydride long remains liquid, and solidifies at about $+15^\circ$, volatilises at 40° , and has a specific gravity 1.94 at 16° . The infusible anhydride, obtained by keeping the ordinary anhydride, has the appearance of silky crystals, which many chemists still regard as a polymeric variety, although from Weber's researches it is more likely to be a polyhydrate, $\text{H}_2\text{SO}_4(\text{SO}_3)_n$, as was stated above.

⁴⁴ Pyrosulphuric chloranhydride, or **pyrosulphuryl chloride**, $\text{S}_2\text{O}_5\text{Cl}_2$, corresponds with pyrosulphuric acid, in the same way that sulphuryl chloride, SO_2Cl_2 , corresponds with sulphuric acid. With SO_3 the latter gives $\text{S}_2\text{O}_5\text{Cl}_2 = \text{SO}_2\text{Cl}_2 + \text{SCl}_3$. It is also obtained by the action of the vapour of sulphuric anhydride on sulphur chloride: $\text{S}_2\text{Cl}_2 + 5\text{SO}_3 = 5\text{SO}_2 + \text{S}_2\text{O}_5\text{Cl}_2$. It (and not sulphuryl chloride, SO_2Cl_2 , Michaelis) is also formed by the action of phosphorus pentachloride in excess on sulphuric acid (or its first chloranhydride, SHO_3Cl). It is an oily liquid, boiling at about 150° , and of sp. gr. 1.8. According to Kononoff (Chap. VII.), its vapour density is normal. It should be noticed that the same substance is obtained by the action of sulphuric anhydride on sulphur tetrachloride, and also on carbon tetrachloride, and this substance is the last product of the metalepsis of CH_4 , and therefore the comparison of SCl_2 and S_2Cl_2 with products of metalepsis (see later) also finds confirmation in particular reactions. Rose, who obtained pyrosulphuryl chloride, $\text{S}_2\text{O}_5\text{Cl}_2$, regarded it as $\text{SCl}_6\cdot 5\text{SO}_3$, for at that time an endeavour was always made to find two component parts of opposite polarity, and this substance was cited as a proof of the existence of a hexachloride, SCl_6 . Pyrosulphuryl chloride is decomposed by cold water, but more slowly than chlorosulphuric acid and the other chloranhydrides.

The relation between pyrosulphuric acid and the normal acid will be obvious if we express the latter by the formula $\text{OH}(\text{SO}_3\text{H})$, because the sulphonic group (SO_3H) is then evidently equivalent to OH , and consequently to H , and if we replace both the hydrogens in water by this radicle we shall obtain $(\text{SO}_3\text{H})_2\text{O}$ —that is, pyrosulphuric acid.

hydrates of phosphoric acid (for example, PHO_3 , $\text{H}_4\text{P}_2\text{O}_7$) have, even in aqueous solution, independent reactions which distinguish them and their salts from the perfect hydrates.

Sulphuric acid, H_2SO_4 , is formed by the combination of its anhydride, SO_3 , and water, with the evolution of a large amount of heat; the reaction $\text{SO}_3 + \text{H}_2\text{O}$ develops 21,300 heat units. The method of its preparation on a large scale and most of the methods employed for its formation are dependent on the oxidation of sulphurous anhydride and the formation of sulphuric anhydride, which forms sulphuric acid under the action of water. The technical method of its manufacture in lead chambers has been described in Chap. VI. The acid obtained from the lead chambers contains a considerable amount

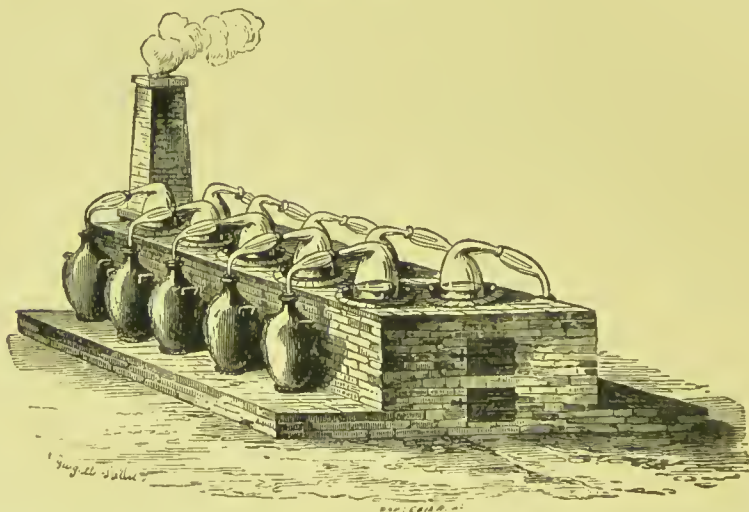


FIG. 98.—Concentration of sulphuric acid in glass retorts. The neck of each retort is attached to a bent glass tube, whose vertical arm is lowered into a glass or earthenware vessel acting as a receiver for the steam which comes over from the acid, as the former still contains a certain amount of acid.

of water, and is also impure owing to the presence of oxides of nitrogen, lead compounds, and certain impurities from the burnt sulphur which have come over in a gaseous and vaporous state (for example, arsenic compounds). For practical purposes, hardly any notice is taken of the majority of these impurities, because they do not interfere with the ordinary properties. Most frequently, endeavours are only made to remove, as far as possible, all the water which can be expelled.⁴⁵ That is, the object is to obtain the hydrate, H_2SO_4 , from the dilute acid (60 per cent.), and this is effected by evaporation by means of heat.

⁴⁵ The removal of the water, or concentration to almost the real acid, H_2SO_4 , is effected for two reasons: in the first place to avoid the expense of transit and in the second place because many processes—for instance, the refining of petroleum—require a strong acid free from an excess of water, the weak acid having no action.

All the aqueous solutions of sulphuric acid begin to part with a certain amount of aqueous vapour when heated to a certain definite temperature. At a low temperature either there is no evaporation of water, or there can even be an absorption of moisture from the air. As the removal of the water proceeds, the vapour pressure of the residue decreases for the same temperature, and therefore the more dilute the acid the lower the temperature at which it gives up a portion of its water. In consequence of this, the removal of water from dilute solutions of sulphuric acid may be easily carried on (up to 75 per cent. H_2SO_4) in lead vessels, because at low temperatures dilute sulphuric acid does not attack lead. But as the acid becomes more concentrated the temperature at which the water comes over becomes higher and higher, and

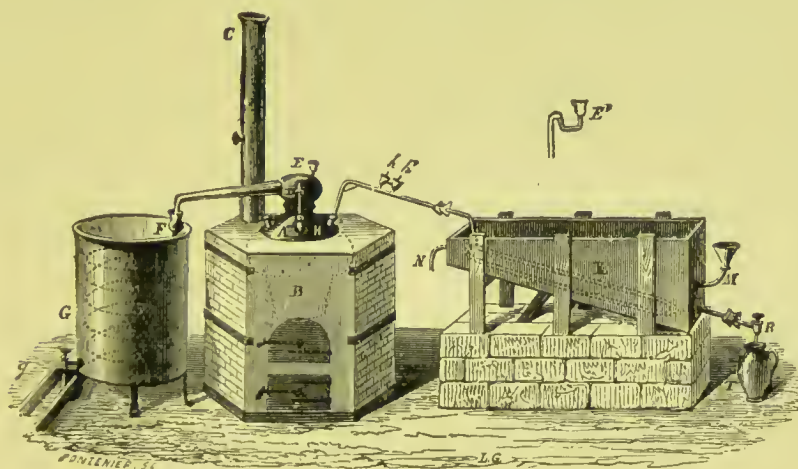


FIG. 99.—Concentration of sulphuric acid in platinum retorts.

then the acid begins to act on lead (with the evolution of sulphuretted hydrogen and conversion of the lead into sulphate), and therefore lead vessels cannot be employed for the complete removal of the water. For this purpose the evaporation is generally carried on in glass or platinum retorts, like those depicted in figs. 98 and 99.

The concentration of sulphuric acid in glass retorts is not a continuous process, and consists of heating the dilute 75 per cent. acid until it ceases to give off aqueous vapour, and until acid containing 93–98 per cent. H_2SO_4 is obtained—and this takes place when the temperature reaches 320° and the density of the residue attains a value 1.847 (66° Baumé).⁴⁶ The platinum vessels designed for the continuous

⁴⁶ The difficulty which which the last portions of water are removed is seen from the fact that the boiling becomes very irregular, totally ceasing at one moment, then suddenly starting again, with the rapid formation of a considerable amount of steam, and at the same time bumping and even overturning the vessel in which it is held. Hence it is not a rare occurrence for the glass retorts to break during the distillation; this causes platinum retorts to be preferred, as the boiling then proceeds quite uniformly.

concentration of sulphuric acid consist of a still B, furnished with a still head E, a connecting pipe E F, and a syphon tube H B, which draws off the sulphuric acid concentrated in the boiler. A stream of sulphuric acid previously concentrated in lead retorts to a density of about 60° Baumé—i.e., to 75 per cent. or a sp. gr. of 1.7—runs continuously into the retort through a syphon funnel E. The apparatus is fed from above, because the acid freshly supplied is lighter than that which has already lost water, and also because the water is more easily evaporated from the freshly supplied acid at the surface. The platinum retort is heated, and the steam coming off⁴⁷ is condensed in a worm F G, while as fresh dilute acid is supplied to the boiler, the acid already concentrated is drawn off through the syphon tube H B, which is furnished with a regulating cock by means of which the outflow of the concentrated acid from the bottom of the retort can be so regulated that it will always present one and the same specific gravity, corresponding with the strength required. For this purpose the acid flowing from the syphon is collected in a receiver, R, in which a hydrometer, indicating its density, floats; if its density is less than 66° Baumé, the regulating cock is closed sufficiently to retard the outflow of sulphuric acid, so as to lengthen the time of its evaporation in the retort.⁴⁸

⁴⁷ According to Regnault, the vapour pressures (in millimetres of mercury) of the water given off by the hydrates of sulphuric acid, $\text{H}_2\text{SO}_4, n\text{H}_2\text{O}$, are—

	$t = 5^\circ$	15°	30°
$n = 1$	0.1	0.1	0.2
2	0.4	0.7	1.5
3	0.9	1.6	4.1
4	1.3	2.8	7.0
5	2.1	4.2	10.7
7	3.2	6.2	15.6
9	4.1	8.0	19.6
11	4.4	9.0	22.2
17	5.5	10.6	26.1

With 89–98.6 per cent. H_2SO_4 the vapour pressure of the water is not observable even at 100° (Knitsch). The boiling-point under the atmospheric pressure, i.e., the temperature of evolution of aqueous vapour, rises with the amount of H_2SO_4 , and for 98.5 per cent. acid is 317° . If the strength of the acid is still greater, SO_3 is given off and the normal (100 per cent.) hydrate H_2SO_4 boils at 245° and the solution containing 26 per cent. of anhydride dissolved in H_2SO_4 boils at 125° .

According to Lunge, the vapour pressure of the aqueous vapour given off from solutions of sulphuric acid containing p per cent. of H_2SO_4 , at t° , equals the barometric pressure—720 to 730 mm.:

$p =$	10	20	30	40	50	60	70	80	85	90	95
$t =$	102°	105°	108°	114°	124°	141°	170°	207°	233°	262°	295°

The latter figures give the temperature at which water is easily expelled from solutions of sulphuric acid of different strengths. But the evaporation begins sooner, and concentration may be carried on at lower temperatures if a stream of air be passed through the acid. Kessler's process is based upon this (note 48).

⁴⁸ The greatest part of the sulphuric acid is used for purposes in which an acid having

The great bulk of the lead chambers in which the 60 per cent. sulphuric acid is made, the waste of nitric acid, and the necessity of further concentrating the acid to a content of 97 per cent. H_2SO_4 render the manufacture of sulphuric acid complicated and costly. The researches of Phillips (1831), Wöhler (1852), Winkler (1875), and others on the formation of sulphuric anhydride (from SO_2 and oxygen) by contact with platinum or the oxides of iron, chromium, &c. have therefore been made the starting-point for the manufacture of sulphuric acid by the **contact process**. These endeavours were only crowned with success at the very close of the last century, thanks to the working out of all the technical details of the process, chiefly by Knitsch (1899) at the chemical works at Ludwigshaven (near the Rhine). In 1900 the Baden Aniline and Soda Works prepared 116,000 tons of sulphuric acid by this process at a less cost than chamber acid. Just as in the chamber process, the raw material here consists of a mixture of air and the gases produced by roasting FeS_2 , ZnS , PbS , and other metallic sulphides, and containing about $7\frac{1}{2}$ per cent. of SO_2 . The contact

a density of 60° Baumé is amply sufficient. Chamber acid has a density up to 1.57 or 50° to 51° Baumé; it contains about 35 per cent. of water. About 15 per cent. of this water can be removed in leaden stills, and nearly all the remainder may be expelled in glass or platinum vessels. Acid of 66° Baumé = 1.847 , contains about 96 per cent. of the hydrate H_2SO_4 . The density falls with a greater or less proportion of water, the maximum density corresponding with $97\frac{1}{2}$ per cent. of the hydrate H_2SO_4 . The concentration of H_2SO_4 in platinum retorts has the disadvantage that sulphuric acid, upwards of 90 per cent. in strength, does corrode platinum, although but slightly (a few grams per tens of tons of acid). The retorts therefore require repairing, and the cost of the platinum exceeds the price obtained for concentrating the acid from 90 per cent. to 98 per cent. This inconvenience has lately (1891, by Matthey) been eliminated by coating the inside of the platinum retorts with a thin (0.1 to 0.02 mm.) layer of gold which is 40 times less corroded by sulphuric acid than platinum. Négrier (1890) carries on the distillation in porcelain dishes, Blond by heating a thin platinum wire immersed in the acid by means of an electric current, but the most profitable methods are that of Kessler (1891) and others of the same kind which consist in passing hot air over sulphuric acid flowing in a thin stream in stone vessels, so that there is no boiling but only evaporation at moderate temperatures.

When, by evaporation of the water, sulphuric acid attains a density of 66° Baumé (sp. gr. 1.84), it is impossible to concentrate it further, because it then distils over unchanged. **The distillation of sulphuric acid** is not generally carried on on a large scale, but forms a laboratory process, employed when particularly pure acid is required. The distillation is effected either in platinum retorts furnished with corresponding condensers and receivers, or in glass retorts. In the latter case, great caution is necessary because the boiling of sulphuric acid itself is accompanied by even more violent jerks and greater irregularity than the evaporation of the last portions of water contained in the acid. Generally the heating is not effected from below, but at the sides of the retort. The evaporation then does not proceed in the whole mass, but only from the upper portions of the liquid, and therefore goes on much more quietly. The acid may also be made to boil quietly by surrounding the retort with good conductors of heat—for example, iron filings, or by immersing a bunch of platinum wires in the acid, as the bubbles of sulphuric acid vapour then form on the extremities of the wires.

material employed is platinised asbestos,^{48a} which lasts for an indefinite time. It is *loosely* laid on perforated sheets attached to an upright support in vertical iron tubes through which the mixture of air and SO_2 is made to pass. Besides the presence of an excess of oxygen a temperature of about 380° to 450° is necessary for the complete and rapid conversion of SO_2 into SO_3 . The reaction proceeds slowly at a lower temperature, while a considerable amount of the SO_3 formed is decomposed at a higher temperature as the reaction, $\text{SO}_2 + \text{O} = \text{SO}_3$, is reversible and evolves heat (see above). Hence the application of heat is only requisite at the beginning, while afterwards it may even be necessary to cool the tubes with water, should the temperature rise above 450° . The resultant SO_3 is absorbed (from its admixture with nitrogen and excess of oxygen) by water, or, better still, by sulphuric acid. In this manner a strong acid (98 per cent. H_2SO_4) or the anhydride itself may be obtained direct without the necessity of concentration. It is therefore extremely probable that this process will in time quite oust the chamber process, owing to its cheapness and simplicity.^{48b}

Strictly speaking, sulphuric acid is not volatile, and at its so-called boiling-point it really decomposes into its anhydride and water, its boiling-point (338°) being nothing else than its temperature of decomposition. The products of this decomposition are substances boiling much below the temperature of the decomposition of sulphuric acid. This conclusion with regard to the process of the distillation of sulphuric acid may be deduced from Bineau's observations on the vapour density of sulphuric acid. This density referred to hydrogen proved to be half that which sulphuric acid should have according to its molecular weight, H_2SO_4 , namely 49, the observed density being 24.5. Besides

^{48a} The asbestos fibre is first immersed in a solution of PtCl_4 and then in one of NH_4Cl . A precipitate containing platinum is thus deposited on the fibres which are then dried and calcined. This leaves a coating of platinum black or finely divided platinum (about 4 per cent. by weight) on the fibres, which renders them catalytic. The platinised asbestos soon loses its power if the gases acting on it contain any traces of arsenic or mercury, as the latter settle on the platinum. And as pyrites always contain some arsenic, the gases obtained from roasting them have first to be very carefully mixed (by means of a jet of steam), cooled and washed in water and sulphuric acid. This apparently trivial fact for a long time prevented the contact method from being profitable.

It should be remembered that the oxides of nitrogen also serve as a contact substance in the chamber process, just like platinum in the present case, only the latter is solid and non-volatile, whereas the oxides of nitrogen are gaseous and therefore easily lost.

^{48b} Strong 98 per cent. sulphuric acid may be conveniently kept in cast-iron vessels, but the fuming acid cannot, because they crack after a time. This is probably due to the presence of cavities in the cast iron in which gases, produced by the SO_3 acting upon the iron, accumulate and produce pressure and rupture. Forged iron vessels are therefore used for keeping this kind of acid.

which, Marignac showed that the first portions of the sulphuric acid distilling over contain less of the elements of water than the portion which remains behind, or which distils over towards the end. This is explained by the fact that on distillation the sulphuric acid is decomposed, but a portion of the water proceeding from its decomposition is retained by the remaining mass of sulphuric acid, and therefore at first a mixture of sulphuric acid and sulphuric anhydride—i.e., fuming sulphuric acid—is obtained in the distillate. It is possible by repeating the distillation several times and only collecting the first portions of the distillate to obtain a distinctly fuming acid. To obtain the definite hydrate H_2SO_4 , it is necessary to refrigerate a highly concentrated acid, of as great a purity as possible, to which a small quantity of sulphuric anhydride has been previously added. Sulphuric acid containing a small quantity (a fraction of a per cent. by weight) of water only freezes at a very low temperature, while the pure normal acid, H_2SO_4 , solidifies when it is cooled below 0° , and therefore the normal acid first crystallises out from the concentrated sulphuric acid. By repeating the refrigeration several times, and pouring off the unsolidified portion, it is possible to obtain a pure **normal hydrate**, H_2SO_4 , which melts at 10.4° . Even at 40° it gives off distinct fumes—that is, it begins to evolve sulphuric anhydride, and therefore even in a dry atmosphere the hydrate H_2SO_4 becomes weaker, until it contains $98\frac{1}{2}$ per cent. H_2SO_4 and $1\frac{1}{2}$ of water.⁴⁹

⁴⁹ Thus it appears that so common, and apparently so stable, a compound as sulphuric acid decomposes even at a low temperature with separation of the anhydride, but this decomposition is restricted by a limit, corresponding to the presence of about $1\frac{1}{2}$ per cent. of water, or to a composition of nearly $\text{H}_2\text{O}, 12\text{H}_2\text{SO}_4$.

Now there is no reason for thinking that this substance is a definite compound; it is an equilibrated system which does not decompose, under ordinary circumstances, below 338° . Dittmar carried on the distillation under pressures varying between 30 and 2,140 millimetres (of mercury), and he found that the composition of the residue hardly varies, and contains from 99.2 to 98.2 per cent. of the normal hydrate, although at 30 mm. the temperature of distillation is about 210° and at 2,140 mm. it is 382° . Furthermore, it is a fact of practical importance that under a pressure of two atmospheres the distillation of sulphuric acid proceeds very quickly.

Sulphuric acid may be **purified** from the majority of its impurities by distillation, if the first and last portions of the distillate be rejected. The first portions will contain the oxides of nitrogen, hydrochloric acid, &c., and the last portions the less volatile impurities. The oxides of nitrogen may be removed by heating the acid with charcoal, which converts them into volatile gases. Sulphuric acid may be freed from arsenic by heating it with manganese dioxide and then distilling. This oxidises all the arsenic into non-volatile arsenic acid. Without a preliminary oxidation it would partially remain as volatile arsenious acid, and might pass over into the distillate. The arsenic may also be driven off by first reducing it to arsenious acid, and then passing hydrochloric acid gas through the heated acid. It is then converted into arsenious chloride, which volatilises. Chamber acid always contains arsenic, but that prepared by the contact method (note 48a) is usually free from arsenic.

In a concentrated form sulphuric acid is commercially known as oil of vitriol, because for a long time it was obtained from green vitriol and has an oily appearance. When mixed with water, sulphuric acid develops a very considerable amount of heat.⁵⁰

Besides the normal hydrate, H_2SO_4 , another definite hydrate, $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ (84.48 per cent. of the normal hydrate, and 15.52 per cent. of water) is known; it crystallises^{50a} extremely easily in large six-

⁵⁰ The amount of heat developed by the mixture of sulphuric acid with water is expressed in the diagram on p. 74, Volume I., by the middle curve, the abscissæ being the percentage amounts of acid (H_2SO_4) in the resultant solution, and the ordinates the numbers of units of heat corresponding with the formation of 100 cubic centimetres of the solution (at 18°). The calculations on which the curve is designed are based on Thomsen's determinations, which show that 98 grams or a molecular amount of sulphuric acid, in combining with m molecules of water (that is, with $m \times 18$ grams of water), develop the following number of units of heat, R:—

$m =$	1	2	3	5	9	19	49	100	200
R =	6379	9418	11137	13108	14952	16256	16684	16859	17066
$c =$	0.432	0.470	0.500	0.576	0.701	0.821	0.914	0.954	0.975
T =	127°	149°	146°	121°	82°	45°	19°	9°	5°

c representing the specific heat of $\text{H}_2\text{SO}_4 \cdot m\text{H}_2\text{O}$ (according to Marignac and Pfaundler), and T the rise in temperature which proceeds from the mixture of H_2SO_4 with $m\text{H}_2\text{O}$. The diagram shows that contraction and rise of temperature proceed almost parallel with each other.

^{50a} Pickering (1890) showed (a) that dilute solutions of sulphuric acid containing up to $\text{H}_2\text{SO}_4 + 10\text{H}_2\text{O}$ deposit ice at -0.12° when there is $2000\text{H}_2\text{O}$ per H_2SO_4 , at -0.23° when there is $1000\text{H}_2\text{O}$, at -1.04° when there is $200\text{H}_2\text{O}$, at -2.12° when there is $100\text{H}_2\text{O}$, at -4.5° when there is $50\text{H}_2\text{O}$, at -15.7° when there is $20\text{H}_2\text{O}$, and at -61° when the composition of the solution is $\text{H}_2\text{SO}_4 + 10\text{H}_2\text{O}$; (b) that for higher concentrations crystals separate out at a considerable degree of cold, having the composition $\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$, and melting at -24.5° , and if either water or H_2SO_4 is added to this compound the temperature of crystallisation falls, so that a solution of the composition $12\text{H}_2\text{SO}_4 + 100\text{H}_2\text{O}$ gives crystals of the above hydrate at -70° , $15\text{H}_2\text{SO}_4 + 100\text{H}_2\text{O}$ at -47° , $30\text{H}_2\text{SO}_4 + 100\text{H}_2\text{O}$ at -32° , $40\text{H}_2\text{SO}_4 + 100\text{H}_2\text{O}$ at -52° ; (c) that if the amount of H_2SO_4 is still greater, a hydrate $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ separates out and melts at $+8.5^\circ$, while the addition of water or sulphuric acid to it lowers the temperature of crystallisation, so that the crystallisation of $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ from a solution of the composition $\text{H}_2\text{SO}_4 + 1.73\text{H}_2\text{O}$ takes place at -22° , from $\text{H}_2\text{SO}_4 + 1.5\text{H}_2\text{O}$ at -6.5° , $\text{H}_2\text{SO}_4 + 1.2\text{H}_2\text{O}$ at $+3.7^\circ$, $\text{H}_2\text{SO}_4 + 0.75\text{H}_2\text{O}$ at $+2.8^\circ$, $\text{H}_2\text{SO}_4 + 0.5\text{H}_2\text{O}$ at -16° ; (d) that when there is less than $40\text{H}_2\text{O}$ per $100\text{H}_2\text{SO}_4$, refrigeration separates out the normal hydrate H_2SO_4 , which melts at $+10.35^\circ$, and that a solution of the composition $\text{H}_2\text{SO}_4 + 0.35\text{H}_2\text{O}$ deposits crystals of this hydrate at -34° , $\text{H}_2\text{SO}_4 + 0.10\text{H}_2\text{O}$ at -4.1° , $\text{H}_2\text{SO}_4 + 0.05\text{H}_2\text{O}$ at $+4.9^\circ$, while fuming acid of the composition $\text{H}_2\text{SO}_4 + 0.05\text{SO}_3$ deposits H_2SO_4 at about $+7^\circ$. Thus, the temperature of the separation of crystals clearly distinguishes the above four regions of solutions, and in the space between $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}$ and $+25\text{H}_2\text{O}$, there separates out a particular hydrate, $\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$ (discovered by Pickering), the isolation of which deserves full attention and further research. I may add here that the existence of a hydrate $\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$ was pointed out in my work, *The Investigation of Aqueous Solutions*, p. 120 (1887), upon the basis that it has at all temperatures a smaller value for the coefficient of expansion, k , in the formula, $S_t = S_0(1 - kt)$, than the adjacent (in composition) solutions of sulphuric acid. And for solutions approximating to $\text{H}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ in their composition, k is constant at all temperatures (for more dilute solutions the value of k increases with t and for more concentrated solutions it decreases). This solution (with $10\text{H}_2\text{O}$) forms the point of transition between more dilute solutions

sided prisms, which form above 0° —namely, at about $+8.5^\circ$; when heated at 210° it loses water.⁵¹ If the hydrates H_2SO_4 and $\text{H}_2\text{SO}_4, \text{H}_2\text{O}$ exist at low temperatures as definite crystalline compounds, and if pyrosulphuric acid, $\text{H}_2\text{SO}_4, \text{SO}_3$, has the same property, and if they all decompose with more or less ease on a rise of temperature, with the disengagement of either SO_3 or H_2O , and in their ordinary form present all the properties of simple solutions, it follows that between sulphuric anhydride, SO_3 , and water, H_2O , there exists a consecutive series of homogeneous liquids or solutions, among which we must distinguish *definite compounds*, and therefore it is quite justifiable to look for other definite compounds between SO_3 and H_2O , beyond the conditions for a change of state. In this respect we may be guided by the variation of properties of any kind, proceeding concurrently with a variation in the composition of a solution.

which deposit ice (water) when refrigerated and those which give crystals of $\text{H}_2\text{SO}_4, 4\text{H}_2\text{O}$. The researches of Knitsch (1901) on the melting-points of strong and fuming sulphuric acids show that there are four maxima alternated by three minima between $\text{H}_2\text{SO}_4, \text{H}_2\text{O}$ and SO_3 , and namely:—

Composition	Melting-point
$\text{H}_2\text{SO}_4, \text{H}_2\text{O}$	$+ 8^\circ$ (max.)
$(\text{H}_2\text{SO}_4)_2, \text{H}_2\text{O}$	$- 35^\circ$ (min.)
H_2SO_4	$+ 10^\circ$ (max.)
$\text{SO}_3, (\text{H}_2\text{SO}_4)_1$	$- 11^\circ$ (min.)
$\text{SO}_3, (\text{H}_2\text{SO}_4)_1$	$+ 34^\circ$ (max.)
$(\text{SO}_3)_2, \text{H}_2\text{SO}_4$	$- 0.8^\circ$ (min.)
SO_3 (polymerised)	$+ 40^\circ$ (max.)

Definite compounds are now supposed by many to correspond to the higher temperatures only, whilst the lower temperatures belong to eutectic mixtures (see Chap. I., note 58). But here, as in many other cases (especially with metallic alloys), these points correspond to substances having a definite molecular (simple) composition. I therefore hold that a strictly definite composition and simple relation in the number of molecules, similar to those of true definite compounds, correspond in many, if not all, cases to the eutectic points. The reason for this must be sought in the dependence of all physico-mechanical properties on those forces and relations which are determined by chemical reaction—i.e., on the mass of the reacting chemical particles. If anywhere between two definite compounds having a maximum t there lies a composition with a minimum t , it may, I think, be most readily explained by some simple relation between the number of particles of the component substances, for all their properties must be connected with their molecular weight. Such is the spirit of all chemical doctrines since the establishment of the conceptions of atoms, molecules, periodicity, &c. The phenomena exhibited between water and sulphuric acid should be kept in mind in the investigation of solutions and alloys. Everything is not clear even here, but still there is much that is clearer than in other solutions or in alloys.

⁵¹ With an excess of snow, the hydrate $\text{H}_2\text{SO}_4, \text{H}_2\text{O}$, like the normal hydrate, gives a freezing mixture, owing to the absorption of a large amount of heat (the latent heat of fusion). In melting, the molecule H_2SO_4 absorbs 960 heat units, and the molecule $\text{H}_2\text{SO}_4, \text{H}_2\text{O}$, 3,680 heat units. If therefore we mix one gram molecule of this hydrate with seventeen gram molecules of snow, there is an absorption of 18,080 heat units, because $17\text{H}_2\text{O}$ absorbs $17 \times 1,430$ heat units, and the combination of the monohydrate with water evolves 9,800 heat units. As the specific heat of the resultant compound $\text{H}_2\text{SO}_4, 18\text{H}_2\text{O}$ is 0.813, the fall of temperature will be 52.6° . And in fact a very low temperature may be obtained by means of sulphuric acid.

But only a few properties have been determined with sufficient accuracy. In those properties which have been determined for many solutions of sulphuric acid, it is actually seen that the above-mentioned definite compounds are distinguished by distinctive marks of change. As an example we may cite the variation of the specific gravity with a variation of temperature (namely, $K=ds/dt$, if s be the sp. gr. and t the

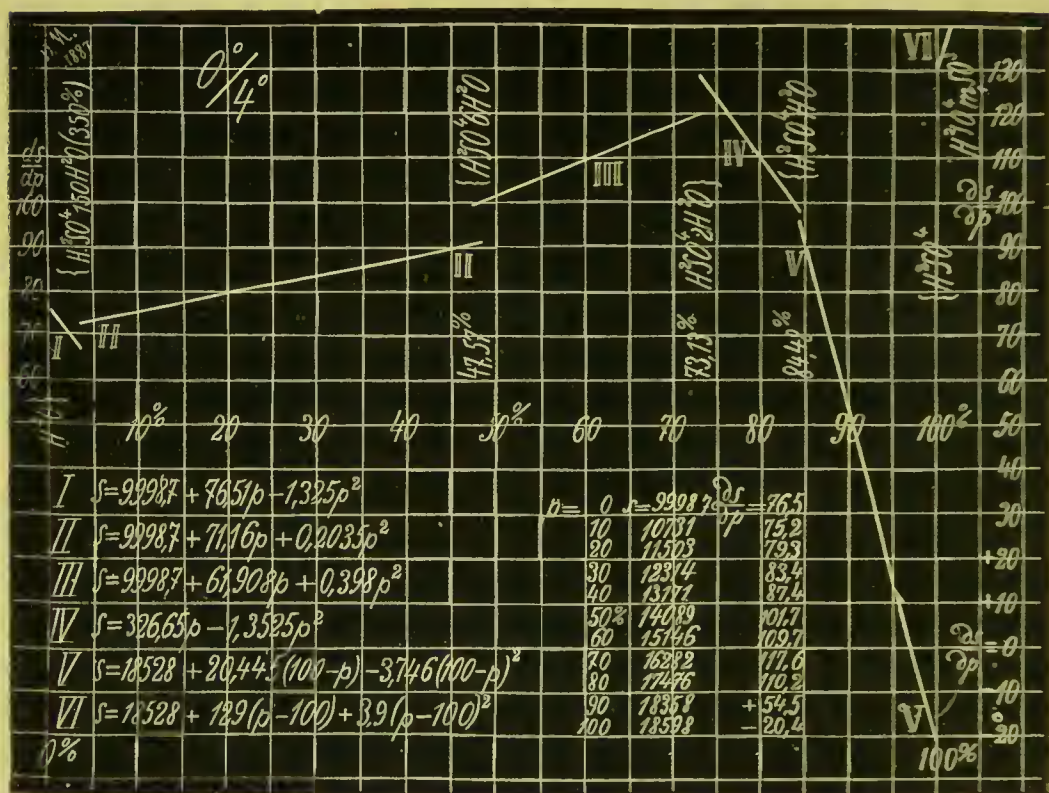


FIG. 100.—Diagram showing the variation of the factor (ds/dp) of the specific gravity of solutions of sulphuric acid. The percentage quantities of the acid, H_2SO_4 , are laid out on the axes of abscissæ. The ordinates are the factors or rises in sp. gr. (water at $4^\circ = 10,000$) with the increase in the quantity of H_2SO_4 .

temperature). For the normal hydrate, H_2SO_4 , this factor is easily determined from the fact that

$$s = 18528 - 10.65t + 0.013t^2,$$

where s is the specific gravity at t (degrees Celsius), the sp. gr. of water at 4° being 10,000. Therefore $K = 10.65 - 0.026t$. This means that at 0° the sp. gr. of the acid H_2SO_4 decreases by 10.65 for every rise of a degree of temperature, at 10° by 10.39, at 20° by 10.13, and at 30° by 9.87.⁵² And for solutions containing slightly more anhydride than the

⁵² For example, if it be taken that at 19° the sp. gr. of pure sulphuric acid is 1.8330, at 20° it will be $1.8330 - (20 - 19)10.13 = 1.8320$.

acid H_2SO_4 (i.e., for fuming sulphuric acid), as well as for solutions containing more water, K is greater than for the acid H_2SO_4 . Thus, for the solution $\text{SO}_3, 2\text{H}_2\text{SO}_4$ at 10° , $K=11.0$. On diluting the acid H_2SO_4 , K again increases until the formation of the solution $\text{H}_2\text{SO}_4, \text{H}_2\text{O}$ (for which $K=11.1$ at 10°), and then, on further dilution with water, it again decreases. Consequently both the hydrates H_2SO_4 and $\text{H}_2\text{SO}_4, \text{H}_2\text{O}$ are here expressed by an alteration of the magnitude of K .

This shows that in solutions it is possible, by studying the variation of their properties (without a change of physical state), to recognise the presence or formation of definite hydrate compounds, and therefore an exact investigation of the properties of solutions, of their specific gravity for instance, should give direct indications of such compounds.⁵³ The mean result of the most trustworthy determinations of this nature is given in the following tables. The first of these tables gives the specific gravities (*in vacuo*, taking the sp. gr. of water at 4° as 1), at 0° , 15° and 30° ,^{53a} for solutions having the composition $\text{H}_2\text{SO}_4 + n\text{H}_2\text{O}$ (the value of n is given in the first column), and contains p (column 2) per cent. (by weight *in vacuo*) of H_2SO_4 .

n	p	0°	15°	30°
100	5.16	1.0374	1.0341	1.0292
50	9.82	1.0717	1.0666	1.0603
25	17.88	1.1337	1.1257	1.1173
15	26.63	1.2040	1.1939	1.1837
10	35.25	1.2758	1.2649	1.2540
8	40.50	1.3223	1.3110	1.2998
6	47.57	1.3865	1.3748	1.3632
5	52.13	1.4301	1.4180	1.4062
4	57.65	1.4881	1.4755	1.4631
3	64.47	1.5635	1.5501	1.5370
2	73.13	1.6648	1.6500	1.6359
1	84.48	1.7940	1.7772	1.7608
0.5	91.59	1.8445	1.8284	1.8128
H_2SO_4	100	1.8529	1.8372	1.8221

⁵³ Unfortunately, notwithstanding the great number of fragmentary and systematic researches which have been made (by Parkes, Ure, Bineau, Kolbe, Lungo, Marignac, Kremers, Thomsen, Perkin, and others) for determining the relation between the sp. gr. and composition of solutions of sulphuric acid, they contain discrepancies which amount to, and even exceed, 0.002 in the sp. gr. For instance, at 15.4° the solution of composition $\text{H}_2\text{SO}_4, 3\text{H}_2\text{O}$ has a sp. gr. 1.5493 according to Perkin (1886), 1.5501 according to Pickering (1890), and 1.5525 according to Lunge (1890). So that the specific gravities given in the adjoining tables are only the average and most probable data in which the error, especially for the 30–80 per cent. solutions, may be not less than 0.0010 (taking water at 4° as 1).

^{53a} Judging from the best existing determinations (of Marignac, Kremers, and Pickering) for solutions of sulphuric acid (especially those containing more than 5 per cent.

In the second table the first column gives the percentage amount p (by weight) of H_2SO_4 ; the second, the weight in grams (S_{15}) of a litre of the solution at 15° (at 4° the weight of a litre of water is 1000 grams); the third, the variation (dS/dt) of this weight for a rise of 1° ; the fourth, the variation dS/dp of this weight (at 15°) for a rise of 1 per cent. of H_2SO_4 ; the fifth, the difference between the weight of a litre at 0° and 15° ($S_0 - S_{15}$), and the sixth column, the difference between the weight of a litre at 15° and 30° ($S_{15} - S_{30}$).

p	S_{15}	dS_{15}/dt	dS_{15}/dp	$S_0 - S_{15}$	$S_{15} - S_{30}$
0	999.15	0.148	7.0	0.7	3.4
5	1033.0	0.27	6.8	3.1	5.0
10	1067.7	0.38	7.1	5.2	6.4
20	1141.9	0.58	7.7	8.6	8.9
30	1221.3	0.69	8.2	10.4	10.4
40	1306.6	0.75	8.8	11.3	11.2
50	1397.9	0.79	9.9	11.9	11.8
60	1501.2	0.86	10.8	13.0	12.7
70	1613.1	0.93	11.6	14.1	13.8
80	1731.4	1.04	11.0	15.8	15.4
90	1819.9	1.08	5.4	16.4	16.0
95	1837.6	1.03	+1.7	15.8	15.1
100	1837.2	1.03	-1.9 ⁵⁴	15.7	15.1

The figures in these tables give the means of finding the amount of H_2SO_4 contained in a solution from its specific gravity,⁵⁵ and also

of H_2SO_4 within the limits of 0° and 30° (and even to 40°), the variation of the sp. gr. with the temperature, t , may (within the accuracy of the existing determinations) be perfectly expressed by the equation: $S_t = S_0 + At + Bt^2$. It must be added that (1) three specific gravities fully determine the variation of the density with t ; (2) $ds/dt = A + 2Bt$, i.e., the factor of the temperature is expressed by a straight line; (3) the value of A (if p is greater than 5 per cent.) is negative, and numerically much greater than B ; (4) the value of B for dilute solutions containing less than 25 per cent. is negative; for solutions approximating to $\text{H}_2\text{SO}_4, 3\text{H}_2\text{O}$ in their composition it is equal to 0, and for solutions of greater concentration B is positive; (5) the factor ds/dp for all temperatures attains a maximum value about $\text{H}_2\text{SO}_4, \text{H}_2\text{O}$; (6) on dividing ds'/dt by S_0 , and so obtaining the coefficient of expansion k (see note 53), a minimum is obtained near H_2SO_4 and $\text{H}_2\text{SO}_4, 4\text{H}_2\text{O}$, and a maximum at $\text{H}_2\text{SO}_4, \text{H}_2\text{O}$ for all temperatures.

⁵⁴ The factor ds/dp passes through 0, that is, the specific gravity attains a maximum value at about 98 per cent. This was discovered by Kohlrausch, and confirmed by Chertel, Pickering, and others.

⁵⁵ Naturally under the condition that there is no other ingredient besides water, which is sufficiently true. For commercial acid, whose specific gravity is usually expressed in degrees of Baumé's hydrometer, we may add that at 15° —

Specific gravity	1	1.1	1.2	1.3	1.4	1.5	1.6	1.7	1.8
Degree Baumé	0	13	24	33.3	41.2	48.1	54.1	59.5	64.2

66° Baumé (the strongest commercial acid or oil of vitriol) corresponds to a sp. gr. 1.84. By employing the second table (by the method of interpolation) the specific gravity

show that 'special points' in the lines of variation of the specific gravity with the temperature and percentage composition correspond with certain definite compounds of H_2SO_4 with OH_2 . This is best seen in the variation of the factors (dS/dt and dS/dp) with the temperature and composition (columns 3, 4, second table). The factor dS/dp (giving the increase of sp. gr. with an increase of 1 per cent. H_2SO_4) points to the following three facts: (1) In passing from 98 per cent. to 100 per cent. acid the factor is negative, and is at 100 per cent. about -0.0019 (i.e., at 99 per cent. the sp. gr. at 15° is about 1.8391 , and at 100 per cent. about 1.8372 , the amount of H_2SO_4 having increased while the sp. gr. has decreased), but as soon as a certain amount of SO_3 is added to the definite compound H_2SO_4 (and 'fuming' acid formed) the specific gravity rises (for example, for $\text{H}_2\text{SO}_4, 0.136 \text{ SO}_3$, the sp. gr. at 15° is 1.866), that is, the factor becomes positive (and, in fact, greater by $+0.01$), so that the formation of the definite hydrate H_2SO_4 is accompanied by a distinct and considerable break in the continuity of the factor; ^{55a} (2) the factor dS/dp , in increasing in its passage from dilute to concentrated solutions, attains a maximum value (at 15° , about 0.012) at about $\text{H}_2\text{SO}_4, 2\text{H}_2\text{O}$, i.e., at about the hydrate corresponding to the form SX_6 proper to the compounds of sulphur, for $\text{S}(\text{OH})_6 = \text{H}_2\text{SO}_4, 2\text{H}_2\text{O}$; the same hydrate corresponds to the composition of gypsum, $\text{CaSO}_4, 2\text{H}_2\text{O}$, and to it also corresponds the greatest contraction and rise of temperature in mixing H_2SO_4 with H_2O (see Chap. I., note 28); (3) the variation of the factor dS/dp , under certain variations in the composition, proceeds so uniformly and regularly, and is so different from the variation given under other proportions of H_2SO_4 and H_2O , that the sum of the variations of dS/dp is expressed by a series of straight lines, if the values of p be laid along the axis of abscissæ and those of dS/dp along the ordinates. ⁵⁶

at a given temperature (from 0° to 30°) can be found for any percentage amount of H_2SO_4 , and therefore conversely the percentage of H_2SO_4 can be found from the specific gravity.

^{55a} Whether similar (even small) breaks in the continuity of the factor ds/dp exist or not, for other hydrates (for instance, for $\text{H}_2\text{SO}_4, \text{H}_2\text{O}$ and $\text{H}_2\text{SO}_4, 4\text{H}_2\text{O}$) cannot as yet be affirmed, owing to the want of accurate data (note 53). In my investigation of this subject (1887) I admit their possibility, but only conditionally; and now, without insisting upon a similar opinion, I only hold to the existence of a distinct break in the factor at H_2SO_4 , being guided by C. Winkler's observations on the specific gravities of fuming sulphuric acid.

⁵⁶ In 1887, on considering all the existing observations for a temperature 0° , I gave a full scheme of the variation of the factor ds/dp at 0° .

I did not then (1887) give this scheme an absolute value, and now after the appearance of two series of new determinations (Lunge and Pickering in 1890), which disagree in many points, I think it well to state quite clearly that Lunge's and Pickering's new determinations have not added to the accuracy of our data respecting the variation of the sp. gr. of solutions of sulphuric acid, and that this subject deserves (as I mentioned

Thus, for instance, for 15° , at 10 per cent., $dS/dp=0.0071$; at 20 per cent., 0.0077; at 30 per cent., 0.0082; and at 40 per cent., 0.0088; that is, for each 10 per cent. the factor increases by about 0.0006 for the whole of the above range, but beyond this it becomes larger, and then, after passing $\text{H}_2\text{SO}_4, 2\text{H}_2\text{O}$, it begins to fall rapidly. Such changes in the variation of the factor apparently take place at about definite hydrates,^{56a} and especially about $\text{H}_2\text{SO}_4, 4\text{H}_2\text{O}$, $\text{H}_2\text{SO}_4, 2\text{H}_2\text{O}$ and $\text{H}_2\text{SO}_4, \text{H}_2\text{O}$. All this, indicating as it does the special chemical affinity of sulphuric acid for water, although of no small significance for comprehending the nature of solutions (see Chap. I. and Chap. VII.), contains many special points which require detailed investigation, the chief difficulty being that it requires great accuracy in a large number of experimental data.

The great affinity of sulphuric acid for water is also seen from the fact that when the strong acid acts on the majority of organic substances containing hydrogen and oxygen (especially on heating) it very frequently takes up these elements in the form of water. Thus strong sulphuric acid, acting on alcohol, $\text{C}_2\text{H}_6\text{O}$, removes the elements of water from it, and converts it into olefiant gas, C_2H_4 . It acts in a similar manner on wood and other vegetable tissues, which it chars. If a piece of wood is immersed in strong sulphuric acid it turns black. This is owing to the fact that the wood contains carbohydrates, for example, cellulose, $\text{C}_6\text{H}_{10}\text{O}_5$, which give up hydrogen and oxygen as water to the sulphuric acid, leaving charcoal, or a black mass very rich in it.⁵⁷

We have already had frequent occasion to notice the very (in 1887) new and careful elaboration, because it concerns that foremost problem in our science—solutions—and introduces a special method into it—that is, the study of differential variations in a property which is so easily observed as the specific gravity of a liquid.

^{56a} H. Crompton (1888), in his researches on the electrical conductivity of solutions of sulphuric acid, and Tammann, in his observations on their vapour pressure, and Konrilloff (1891), in studying the formation of peroxide of hydrogen in the electrolysis of solutions of sulphuric acid, found a correlation with the hydrates indicated as above by the investigation of their specific gravities. Still, the whole question is so complicated, and the experimental data as yet so imperfect, that neither the number nor exact composition of many hydrates can be considered quite certain.

⁵⁷ Cellulose, for instance, unsized paper or calico, is dissolved by strong sulphuric acid. Acid diluted with about half its volume of water converts it (if the action be of short duration) into vegetable parchment (Chap. I., note 18). The action of dilute solutions of sulphuric acid converts it into hydro-cellulose, and the fibre loses its coherent quality and becomes brittle. The prolonged action of strong sulphuric acid chars the cellulose, while dilute acid converts it into glueose. If sulphuric acid be kept in an open vessel, the organic matter of the dust held in the atmosphere falls into it and blackens the acid. It is evident from the preceding that strong sulphuric acid will act as a powerful poison; whilst, on the other hand, when very dilute, it is employed in certain medicines and as a fertiliser for plants.

energetic acid properties of sulphuric acid, so that we shall now only consider a few of their aspects. First of all, we must remember that, with calcium, strontium, and especially with barium and lead, sulphuric acid forms very slightly soluble salts, whilst with the majority of other metals it gives more easily soluble salts, which in the majority of cases are able, like sulphuric acid itself, to combine with water to form crystallo-hydrates. Normal sulphuric acid, containing two atoms of hydrogen in its molecule, is able for this reason alone to form two classes of salts, **normal** and **acid**, which it does with great facility **with the alkali metals**. The metals of the alkaline earths and the majority of other metals, if they do form acid sulphates, only do so under exceptional conditions (with an excess of strong sulphuric acid), and these salts when formed are decomposable by water—that is, although having a certain degree of physical stability they have no chemical stability. Besides the acid salts, RHSO_4 , sulphuric acid also gives other forms of acid salts. An entire series of salts having the composition $\text{RHSO}_4, \text{H}_2\text{SO}_4$, or for bivalent metals $\text{RSO}_4, 3\text{H}_2\text{SO}_4$,⁵⁸ has been prepared. Such salts have been obtained for potassium, sodium, nickel, calcium, silver, magnesium, and manganese. They are prepared by dissolving the sulphates in an excess of sulphuric acid and heating the solution until the excess of acid is driven off; on cooling, the mass solidifies to a crystalline salt. Besides which, Rose obtained a salt having the composition $\text{Na}_2\text{SO}_4, \text{NaHSO}_4$, and if HNaSO_4 is heated it easily forms a salt, $\text{Na}_2\text{S}_2\text{O}_7 = \text{Na}_2\text{SO}_4, \text{SO}_3$; hence it is clear that sulphuric anhydride combines with various proportions of bases, just as it combines with various proportions of water.

We have already learned that sulphuric acid displaces the acid from the salts of nitric, carbonic, and many other volatile acids. Berthollet's laws (Chap. X.) explain this by the small volatility of sulphuric acid; and, indeed, in aqueous solution sulphuric acid displaces the much less soluble boric acid from its compounds; for instance, from borax, and it also displaces silica from its compounds with bases; but both boric anhydride and silica, when fused with sulphates, decompose them, displacing sulphuric anhydride, SO_3 , because they are less volatile than sulphuric anhydride. It is also well known that with metals, sulphuric acid forms salts, hydrogen (with Fe, Zn, &c.) or sulphur dioxide (with Cu, Hg, &c.) being evolved.^{58a}

⁵⁸ Weber (1884) obtained a series of salts, $\text{R}_2\text{O}, 8\text{SO}_3, n\text{H}_2\text{O}$ for K, Rb, Cs, and Tl.

^{58a} Ditte (1890) divides all the metals into two groups with respect to their behaviour with sulphuric acid: the first group includes silver, mercury, copper, lead, and bismuth, which are only acted upon by hot concentrated acid. In this case sulphurous anhydride is evolved without any by-reactions. The second group contains manganese, nickel, cobalt, iron, zinc, cadmium, aluminium, tin, thallium, and the alkali metals. They react with

The reactions of sulphuric acid with respect to organic substances are generally determined by its acid character, when neither the direct extraction of water, nor oxidation at the expense of the oxygen of the sulphuric acid,⁵⁹ nor disintegration takes place. Thus the majority of the unsaturated hydrocarbons, C_nH_{2m} , form with sulphuric acid a special class of **sulphonic acids**, $C_nH_{2m-1}(HSO_3)$; for example, benzene, C_6H_6 , forms benzenesulphonic acid, $C_6H_5 \cdot SO_3H$. It is evident from the existence of these acids that the hydrogen in organic compounds is replaceable by the group SO_3H , just as it may be replaced by the radicles Cl , NO_2 , CO_2H , and others. As the radicle of sulphuric acid or **sulphoxyl**, SO_2OH or SHO_3 , contains, like carboxyl (Vol. I., p. 419), one hydrogen (as hydroxyl) of the sulphuric acid, the resultant substances are acids whose basicity is equal to the number of hydrogens replaced by sulphoxyl. Since also sulphoxyl takes the place of hydrogen, and itself contains hydrogen, the sulpho-acids are equal to a hydrocarbon + SO_3 , just as every organic (carboxylic) acid is equal to a hydrocarbon + CO_2 . As a matter of fact, many sulphonic acids are obtained by the direct combination of sulphuric anhydride: $C_6H_5(SO_3H) = C_6H_6 + SO_3$. The sulphonic acids give soluble barium salts, and are therefore easily distinguished from sulphuric acid. They are soluble in water and non-volatile, and when distilled give sulphurous anhydride (whilst the hydroxyl previously in combination with the sulphurous anhydride remains in the hydrocarbon group; thus, phenol, $C_6H_5 \cdot OH$, is obtained from benzenesulphonic acid), and they are very energetic, because the hydrogen acting in them is of the same nature as in sulphuric acid itself.⁶⁰

sulphuric acid of any concentration at any temperature. At a low temperature, hydrogen is disengaged, and at higher temperatures (and with very concentrated acid), hydrogen and sulphurous anhydride are simultaneously evolved.

⁵⁹ For example, the action of hot sulphuric acid on nitrogenous compounds, as applied in Kjeldahl's method for the estimation of nitrogen (Volume I., p. 265). It is obvious that when sulphuric acid acts as an oxidising agent it forms sulphurous anhydride.

The action of sulphuric acid on the alcohols is exactly similar to its action on alkalies, because the alcohols, like alkalies, react with acids; a molecule of alcohol with a molecule of sulphuric acid gives off water and forms an *acid* ethereal salt—that is, there is produced an ethereal compound corresponding with acid salts. Thus, for example, the action of sulphuric acid, H_2SO_4 , on ordinary alcohol, C_2H_5OH , gives water and sulphovinic acid, $C_2H_5HSO_4$ —that is, sulphuric acid in which one atom of hydrogen is replaced by the radicle C_2H_5 , of ethyl alcohol, $SO_2(OH)(OC_2H_5)$, or, what is the same thing, the hydrogen in alcohol is replaced by the radicle (sulphoxyl) of sulphuric acid, $C_2H_5O \cdot SO_2(OH)$.

⁶⁰ We shall mention the following difference between the sulphonic acids and the ethereal acid sulphates (note 59): the former re-form sulphuric acid with difficulty and the latter easily. Thus, sulphovinic acid when heated with an excess of water is reconverted into alcohol and sulphuric acid. This is explained in the following manner. Both these classes of acids are produced by the substitution of hydrogen by SO_3H , or the

Sulphuric acid, as containing a large proportion of oxygen, is a substance which frequently acts as an oxidising agent, in which case it is **deoxidised, forming sulphurous anhydride** and water (or even, although more rarely, sulphuretted hydrogen and sulphur). Sulphuric acid acts in this manner on charcoal, copper, mercury, silver, organic and other substances, which are unable to evolve hydrogen from it directly, as we saw in describing sulphurous anhydride.

Although the hydrate of a higher saline form of oxidation (Chap. XV.), sulphuric anhydride is capable of further oxidation, and forms a kind of peroxide, just as hydrogen gives hydrogen peroxide in addition to water, or as sodium and potassium, besides the oxides Na_2O and K_2O , give their peroxides, compounds which are in a chemical sense unstable, powerfully oxidising, and not directly able to enter into saline combinations. If the oxides of potassium, barium, &c., be compared with water, their peroxides must in like manner correspond to hydrogen peroxide,⁶¹ not only because the oxygen contained in them is very mobile and easily liberated, and because their reactions are similar, but also because they can be mutually transformed into each other, and are able to form compounds with each other, with bases and with water, and indeed form a kind of peroxide salts.⁶²

univalent radicle of sulphuric acid, but in the formation of ethereal acid sulphates the SO_3H replaces the hydrogen of the hydroxyl in the alcohol, whilst in the formation of the sulphonic acids the SO_3H replaces the hydrogen of a hydrocarbon. This difference is clearly evidenced in the existence of two acids of the composition $\text{SO}_4\text{C}_2\text{H}_6$. The one, mentioned above, is sulphovinic acid or alcohol, $\text{C}_2\text{H}_5\cdot\text{OH}$, in which the hydrogen of the hydroxyl is replaced by sulphonyl = $\text{C}_2\text{H}_5\cdot\text{OSO}_2\text{H}$, whilst the other is alcohol, in which one atom of the hydrogen in ethyl, C_2H_5 , is replaced by the sulphonic group—that is = $(\text{C}_2\text{H}_4)\text{SO}_3\text{H}\cdot\text{OH}$. The latter is called isethionic acid. It is more stable than sulphovinic acid. The details as to these interesting compounds must be looked for in works on organic chemistry, but I think it necessary to note one of the general methods of formation of these acids. The sulphites of the alkalis—for example, K_2SO_3 —when heated with the halogen products of metalepsis, give a halogen salt and a salt of a sulphonic acid. Thus methyl iodide, CH_3I , derived from marsh gas, CH_4 , when heated to 100° with a solution of potassium sulphite, K_2SO_3 , gives potassium iodide, KI , and potassium methylsulphonate, $\text{CH}_3\text{SO}_3\text{K}$ —that is, a salt of the sulphonic acid. This shows that the sulphonic acid may be referred to sulphurous acid, and that there is a resemblance between sulphuric and sulphurous acid, which is most simply expressed by the fact that in sulphuric acid the sulphonyl is combined with OK , while in sulphurous acid it is combined with H , for $\text{H}_2\text{SO}_3 = \text{H}(\text{HSO}_3)$.

⁶¹ The reaction $\text{BaO} + \text{O}$ develops 12,000 heat units, whilst the reaction $\text{H}_2\text{O} + \text{O}$ absorbs 21,000 heat units.

⁶² Schöne obtained a compound of peroxide of barium with peroxide of hydrogen. If barium peroxide be dissolved in hydrochloric (or acetic) acid, or if a solution of hydrogen peroxide be diluted with a solution of barium hydroxide, a pure hydrate will be precipitated having the composition $\text{BaO}_2\cdot 8\text{H}_2\text{O}$ (sometimes the composition is taken as $\text{BaO}_2\cdot 6\text{H}_2\text{O}$). This fact was already known to Thénard. Schöne showed that if hydrogen peroxide is in excess, a crystalline compound of the two peroxides, $\text{BaO}_2\cdot \text{H}_2\text{O}_2$, is precipitated. Thus, barium peroxide combines with both water and hydrogen peroxide. This is a very important fact for the comprehension of the composition of other peroxides.

This is also the character of **persulphuric acid**, discovered in 1878 by Berthelot, and its corresponding anhydride or **peroxide of sulphur**, S_2O_7 . It is formed from $2SO_3 + O$ with the absorption of heat (-27 thousand heat units), like ozone from $O_2 + O$ (-29 thousand units of heat), or hydrogen peroxide from $H_2O + O$ (-21 thousand heat units).

Peroxide of sulphur is produced by the action of a silent discharge upon a mixture of oxygen and sulphurous anhydride.⁵³ With water S_2O_7 gives persulphuric acid, $H_2S_2O_8$. The latter is obtained more simply by mixing strong sulphuric acid (not weaker than $H_2SO_4, 2H_2O$) directly with hydrogen peroxide, or by the action of a galvanic current on sulphuric acid mixed with a certain amount of water, and cooled, the electrodes being platinum wires, when persulphuric acid naturally appears at the positive pole.⁵⁴ When an acid of the strength $H_2SO_4, 6H_2O$ is taken, at first only the hydrate of the sulphuric peroxide, S_2O_7, H_2O , is formed; but when the concentration about the positive pole reaches $H_2SO_4, 3H_2O$, a mixture of hydrogen peroxide and the hydrate of sulphuric peroxide begins to be formed. Dilute solutions of sulphuric peroxide can be kept better than more concentrated solutions, but the latter may be obtained containing as much as 123 grams of the peroxide to a litre. It is a very instructive fact that

⁵³ Anhydrous **sulphuric peroxide**, S_2O_7 , is obtained by the prolonged (8 to 10 hours) action of a silent discharge of considerable intensity on a mixture of oxygen and sulphurous anhydride; the vapour of sulphuric peroxide, S_2O_7 , condenses as liquid drops or, after being cooled to 0° , in the form of long prismatic crystals, resembling those of sulphuric anhydride. The anhydrous compound, S_2O_7 (and also the hydrated compound), cannot be preserved long, as it splits up into oxygen and sulphuric anhydride. Direct experiment shows that a mixture of equal volumes of sulphurous anhydride and oxygen leaves a residue of $\frac{3}{4}$ of the oxygen taken, which indicates the formula S_2O_7 . This substance is soluble in water, and it then gives a hydrate, probably having the composition $S_2O_7, H_2O = 2SHO_4$.

In order to fully demonstrate the reality of a peroxide form for acids, it should be mentioned that some years ago Brodie obtained the so-called **acetic peroxide**, $(C_2H_3O)_3O_2$, by the action of barium peroxide on acetic anhydride, $(C_2H_3O)_2O$. Its corresponding hydrate is also known. A similar higher oxide has long been known for chromium.

⁵⁴ When an acid of the strength $H_2SO_4, 6H_2O$ is taken, at first only the hydrate of the sulphuric peroxide, S_2O_7, H_2O , is formed, but when the concentration at the positive pole reaches $H_2SO_4, 3H_2O$, a mixture of hydrogen peroxide and the hydrate of sulphuric peroxide begins to be formed. A state of equilibrium is ultimately arrived at when the amounts of these substances correspond with the proportion $S_2O_7 : 2H_2O_2$, which, as it were, answers to a new compound. But its existence cannot be admitted because the sulphuric peroxide can be easily distinguished from the hydrogen peroxide in the solution owing to the fact that the former does not act on an acid solution of potassium permanganate, whilst the hydrogen peroxide disengages both its own oxygen and that of the permanganic acid, which it converts into manganous oxide. Their common property of liberating iodine from an acid solution of the potassium iodide enables the sum of the active oxygen in them both to be determined. Ellbs (1895) found by experiment that most $H_2S_2O_8$ is formed in electrolysis when the sulphuric acid taken has a sp. gr. from 1.35 to 1.5, i.e., with hydrates containing from $+7H_2O$ to $+31H_2O$.

hydrogen peroxide is always formed when strong solutions of persulphuric acid break up on keeping. So that the bond between the two peroxides is established both by analysis and synthesis: hydrogen peroxide is able to produce $S_2H_2O_8$, and the latter to produce hydrogen peroxide. A mixture of sulphuric peroxide with sulphuric acid or water is decomposed, with the evolution of oxygen, either when heated or under the action of spongy platinum. The same thing takes place with a solution of baryta, although at first no precipitate is formed and the decomposition of the barium salt, BaS_2O_8 , with the formation of $BaSO_4$, only proceeds slowly, so that the solution may be filtered (the barium salt of persulphuric acid is soluble in water). Mercury, ferrous oxide, and the stannous salts are oxidised by $S_2H_2O_8$. These are all distinct signs of true peroxides. The same common properties (capacity for oxidising, property of forming peroxide of hydrogen, &c.) are possessed by the alkali salts of persulphuric acid, which are obtained by the action of an electric current upon certain sulphates, for instance, ammonium or potassium sulphate. The ammonium salt of persulphuric acid, $(NH_4)_2S_2O_8$, is especially easily formed by this means, and is now prepared on a large scale and used (like Na_2O_2 and H_2O_2) for bleaching tissues and fibres.⁶⁵

⁶⁵ Marshall (1891) studied the formation of this class of compounds more fully; he subjected a saturated solution of bisulphate of potassium to electrolysis with a current of 3–3½ ampères; before electrolysis, dilute sulphuric acid is added to the liquid surrounding the negative pole, and during electrolysis the solution at the anode is cooled. The electrolysis is continued without interruption for two days, and a crystalline deposit separates at the anode. To avoid decomposition the latter is not filtered through paper, but through a perforated platinum plate, and dried on a porous tile. The mother liquor, with the addition of a fresh solution of bisulphate of potassium, is again subjected to electrolysis, and the crystals formed at the anode are again collected, &c. The salt so obtained may be recrystallised by dissolving it in hot water and rapidly cooling the solution after filtration; a small proportion of the salt is decomposed by this treatment. The composition of the salt is determined either by igniting it, when it forms sulphate of potassium, or else by titrating the active oxygen with permanganate; its composition was found to correspond with the salt of persulphuric acid, $K_2S_2O_8$. The solution of the salt has a neutral reaction, and does not give a precipitate with salts of other metals. $K_2S_2O_8$ is the most insoluble of the salts of persulphuric acid. With nitrate of silver it forms a salt, which gives peroxide of silver under the action of water, according to the equation: $Ag_2S_2O_8 + 2H_2O = Ag_2O_2 + 2H_2SO_4$. With an alkaline solution of a eupric salt (Fehling's solution) it forms a red precipitate of peroxide of copper. Manganese and cobalt salts give precipitates of MnO_2 and Co_2O_3 . Ferrous salts are rapidly oxidised, while potassium iodide slowly disengages iodine at the ordinary temperature. All these reactions indicate the powerful oxidising properties of $K_2S_2O_8$. In oxidising in the presence of water it gives a residue of $KHSO_4$. The decomposition of the dry salt begins at 100°, but is not complete even at 250°. The freshly prepared salt is inodorous, but after being kept in a closed vessel it evolves a peculiar smell different from that of ozone. The ammonium salt, $(NH_4)_2S_2O_8$, is obtained in a similar manner. It is soluble to the extent of 58 parts per 100 parts by weight of water. The decomposition of the ammonium salt by the hydrated oxide of barium gives the barium salt, $BaS_2O_8 \cdot 4H_2O$,

In order to understand the relation of sulphuric peroxide to sulphuric acid we must first remark that hydrogen peroxide is to be considered, in accordance with the law of substitution, as water, $\text{H}(\text{OH})$, in which H is replaced by (OH) . Now the relation of $\text{H}_2\text{S}_2\text{O}_8$ to H_2SO_4 is exactly similar. The radicle of sulphuric acid, equivalent to hydrogen, is HSO_4 ; ^{65a} it corresponds with the (OH) of water, and therefore sulphuric acid, $\text{H}(\text{SHO}_4)$, gives $(\text{SHO}_4)_2$ or $\text{S}_2\text{H}_2\text{O}_8$, in exactly the same manner as water gives $(\text{HO})_2$ —i.e., H_2O_2 .⁶⁶

which is soluble to the extent of 52.2 parts in 100 parts of water at 0° . The crystals do not deliquesce in the air, and decompose in the course of several days. Solutions of the pure salt decompose slowly at the ordinary temperature. To completely decompose this salt it is necessary to boil its solution for a long time. Alcohol dissolves the solid salt; the anhydrous salt does not separate from the alcoholic solution, but a hydrate containing one molecule of water, $\text{BaS}_2\text{O}_8 \cdot \text{H}_2\text{O}$, which is soluble in water but insoluble in absolute alcohol. Sodium barium persulphate decomposes even when slightly heated. The free acid, which may serve for the preparation of other salts, is obtained by treating the barium salt with sulphuric acid. The lead salt, PbS_2O_8 , has been obtained from the free acid; it crystallises with two or three molecules of water. It is soluble in water, deliquesces in the air, and with alkalis gives a precipitate of the hydrated oxide which rapidly oxidises into the binoxide.

Traube, before Marshall's researches, thought that the electrolysis of solutions of sulphuric acid did not give a hydrate of S_2O_7 , but an oxide having the composition SO_4 . On repeating his former researches (1892) Traube considers it very likely that the salts obtained by Marshall corresponded to an acid $\text{H}_2\text{SO}_4 + \text{SO}_4$, i.e., that the indifferent oxide, SO_4 , can combine with sulphuric acid and form peculiar saline compounds. Traube, however, subsequently much doubted the truth of such a conclusion, but it afterwards lay at the basis of Baeyer and Villiger's conclusion (1901) regarding the independent existence of a special acid, $\text{H}_2\text{SO}_5 = \text{H}_2\text{O} + \text{SO}_4$. Lowry and West investigated the same subject somewhat earlier (1900), and came to the conclusion that peroxide of hydrogen gives three degrees of combination— $\text{H}_2\text{O}_2 + 1$ or 2 or 4SO_3 . The first is the H_2SO_5 just mentioned, the second is $\text{H}_2\text{S}_2\text{O}_8$, which is generally recognised, and the third, $\text{H}_2\text{S}_4\text{O}_{14}$, is stated by these authors to be formed in electrolysis. This question cannot yet be considered as decided. The acid having the composition $\text{H}_2\text{SO}_5 = \text{H}_2\text{O}_2 \cdot \text{SO}_3$ is known as 'Caro's reagent or acid,' and was obtained by mixing $\text{H}_2\text{S}_2\text{O}_8$ with dilute sulphuric acid; the resultant acid is highly oxidising, and converts aniline into nitrobenzene, &c. If it be supposed that $\text{H}_2\text{S}_2\text{O}_8$ combines with H_2O_2 , formed from the same persulphuric acid, then the formation of H_2SO_5 may be understood, because $2\text{H}_2\text{SO}_5 = \text{H}_2\text{S}_2\text{O}_8 + \text{H}_2\text{O}_2$. This question requires further study.

^{65a} Or one of those supposed ions which appear at the positive pole in the decomposition of sulphuric acid by the action of a galvanic current.

⁶⁶ If this be true, one would expect the following peroxide hydrates: for phosphoric acid, $(\text{H}_2\text{PO}_4)_2 = \text{H}_4\text{P}_2\text{O}_8 = 2\text{H}_2\text{O} + 2\text{PO}_3$; for carbonic acid, $(\text{HCO}_3)_2 = \text{H}_2\text{C}_2\text{O}_6 = \text{H}_2\text{O} + \text{C}_2\text{O}_5$; and for lead the true peroxide will be also Pb_2O_5 , &c. Judging from the example of barium peroxide (note 62), these peroxide forms will probably combine together. It seems to me that the compounds obtained by Fairley for uranium are very instructive as elucidating the peroxides. In the action of hydrogen peroxide in an acid solution on uranium oxide, UO_3 , there is formed a uranium peroxide, $\text{UO}_4 \cdot 4\text{H}_2\text{O}$ $\text{U} = 240$), but hydrogen peroxide acts on uranium oxide in the presence of caustic soda; on the addition of alcohol a crystalline compound of the composition $\text{Na}_4\text{UO}_8 \cdot 4\text{H}_2\text{O}$ is precipitated, which is doubtless a compound of the peroxides of sodium, Na_2O_2 , and uranium, UO_4 . It is very possible that the first peroxide, $\text{UO}_4 \cdot 4\text{H}_2\text{O}$, contains the elements of hydrogen peroxide and uranium peroxide, U_2O_7 , or even $\text{U}(\text{OH})_6 \cdot \text{H}_2\text{O}_2$, just as the

The largest part of the sulphuric acid made is used for reacting, on sodium chloride in the manufacture of sodium carbonate; for the manufacture of the volatile acids, like nitric, hydrochloric, &c., from their corresponding salts; for the preparation of ammonium sulphate, alums, vitriols (copper and iron), artificial manures, superphosphate (Chap. XIX., note 18) and other salts of sulphuric acid; in the treatment of bone ash for the preparation of phosphorus, and for the solution of metals—for example, of silver in its separation from gold—for cleaning metals from rust, &c. A large amount of oil of vitriol is also used in the treatment of organic substances; it is used for the extraction of stearin, or stearic acid, from tallow, for refining petroleum and various vegetable oils, in the preparation of nitro-glycerine (Chap. VI., notes 37 and 37a), for dissolving indigo and other colouring matters, for the conversion of paper into vegetable parchment, for the preparation of ether from alcohol, for the preparation of various artificial scents from fusel oil, for the preparation of vegetable acids, such as oxalic, tartaric, and citric, for the conversion of non-fermentable starchy substances into fermentable glucose, and in a number of other processes. It would be difficult to find another artificially prepared substance which is so frequently applied in the arts as sulphuric acid. Where there are not works for its manufacture, the economical production of many other substances of great technical importance is impossible. In those localities which have arrived at a high technical activity the amount of sulphuric acid consumed is proportionately large; sulphuric acid, sodium carbonate, and lime are the most important of the artificially prepared agents employed in factories.

Besides the normal acids of sulphur, H_2SO_3 , $\text{H}_2\text{SO}_3\text{S}$, and H_2SO_4 , corresponding with sulphuretted hydrogen, H_2S , in the same way that HClO_3 and HClO_4 correspond with hydrochloric acid, HCl , there exists a peculiar series of acids which are termed **thionic acids**. Their general composition is $\text{S}_n\text{H}_2\text{O}_6$, where n varies from 2 to 5 and 6. If $n=2$, the acid is called dithionic acid. The others are distinguished as trithionic, tetrathionic, pentathionic, and hexathionic acids. Their composition, existence, and reactions are easily understood if they are referred to the class of the sulphonic acids—that is, if their relation to sulphuric acid is expressed in just the same manner as the relation of the organic acids to carbonic acid. The organic acids (Chap. IX.) proceed from the hydrocarbons by the substitution of peroxide form lately discovered by Spring for tin perhaps contains $\text{Sn}_2\text{O}_3, \text{H}_2\text{O}_2$. Melikoff and Pissarjeffsky (1898) confirmed the composition UO_4 . The chemistry of the peroxides is being investigated by many chemists, and L. Pissarjeffsky collected all the most important data on this most interesting subject in his work, *The Peroxides and Per-Acids* (Odessa, 1902).

their hydrogen by carboxyl—that is, by the radicle of carbonic acid, CHO_2 . The formation of the acids of sulphur by means of sulphonyl may be represented in the same manner, $\text{HSO}_3 = \text{H}_2\text{SO}_4 - \text{HO}$. Therefore to hydrogen, H_2 , there should correspond the acids $\text{H} \cdot \text{SHO}_3$, sulphurous, and $\text{SHO}_3 \cdot \text{SHO}_3 = \text{S}_2\text{H}_2\text{O}_6$, or dithionic; to SH_2 there should correspond the acids $\text{SH}(\text{SHO}_3) = \text{H}_2\text{S}_2\text{O}_3$ (thiosulphuric), and $\text{S}(\text{SHO}_3)_2 = \text{H}_2\text{S}_3\text{O}_6$ (trithionic); to S_2H_2 the acids $\text{S}_2\text{H}(\text{SHO}_3) = \text{H}_2\text{S}_3\text{O}_2$ (unknown), and $\text{S}_2(\text{SHO}_3)_2 = \text{H}_2\text{S}_4\text{O}_6$ (tetrathionic); to S_3H_2 , $\text{S}_3(\text{SHO}_3)_2 = \text{H}_2\text{S}_5\text{O}_6$ (pentathionic), and to H_2S_4 , hexathionic acid, $(\text{HSO}_3)_2\text{S}_4 = \text{H}_2\text{S}_6\text{O}_6$.^{66a} We know that iodine reacts directly with the hydrogen of sulphuretted hydrogen and combines with it, and if thiosulphuric acid contains the radicle of sulphuretted hydrogen (or hydrogen united with sulphur) of the same nature as in sulphuretted hydrogen, it is not surprising that iodine reacts with sodium thiosulphate and forms sodium tetrathionate. Thus, thiosulphuric acid, $\text{HS}(\text{SHO}_3)$, when deprived of H , gives a radicle which immediately combines with another similar radicle, forming the tetrathionate, $\text{S}_2(\text{SO}_2\text{HO})_2$. According to this view⁶⁷ of the structure of the thionic acids and salts, it is also clear how all the thionic acids, like thiosulphuric acid, easily give sulphur and sulphides, with the exception only of dithionic acid, $\text{H}_2\text{S}_2\text{O}_6$, which, judging from the above, stands apart from the series of the other thionic acids. Dithionic acid stands in the same relation to sulphuric acid as oxalic acid does to carbonic. Oxalic acid is dicarboxyl, $(\text{CHO}_2)_2 = \text{C}_2\text{H}_2\text{O}_4$, and so also dithionic acid is disulphonyl, $(\text{SHO}_3)_2 = \text{S}_2\text{H}_2\text{O}_6$. Oxalic acid, when ignited, decomposes into carbonic anhydride and carbonic oxide, CO , and dithionic acid, when heated, decomposes into sulphuric anhydride and sulphurous anhydride, SO_2 , and SO_2 stands in the same relation to SO_3 as CO to CO_2 . This also explains the peculiarity of the calcium, barium, and lead, &c. salts of the thionic acids being easily soluble (although the corresponding salts of H_2SO_3 , H_2SO_4 , and H_2S dissolve with difficulty), because the former are similar to the salts of the sulphonyl acids, which are also soluble in water. Thus the thionic acids are **disulphonic acids**, just as many dicarboxylic acids are known—for example, $\text{CH}_2(\text{CO}_2\text{H})_2$, $\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2$.⁶⁸

^{66a} A heptathionic acid, $(\text{HSO}_3)_3\text{S}_5$, should correspond to H_2S_5 , but it has not yet been isolated.

⁶⁷ This view was communicated by me in 1870 to the Russian Chemical Society.

⁶⁸ **Dithionic acid**, $\text{H}_2\text{S}_2\text{O}_6$, is distinguished among the thionic acids as containing the least proportion of sulphur. It is also called hyposulphuric acid, because its supposed anhydride, S_2O_5 , contains more O than sulphurous oxide, SO_2 or S_2O_4 , and less than sulphuric anhydride, SO_3 or S_2O_6 . Dithionic acid, discovered by Gay-Lussac and Welter, is known as a hydrate and in the form of salts, but not as anhydride. The method for preparing dithionic acid usually employed is by the action of finely powdered

Sulphur evidently exhibits an acid character, not only in its compounds with hydrogen and oxygen, but also in those with other elements.

manganese dioxide on a solution of sulphurous anhydride. On shaking, the smell of the latter disappears, and the manganese salt of the acid in question passes into solution; $\text{MnO}_2 + 2\text{SO}_2 = \text{MnS}_2\text{O}_6$. If the temperature is raised, the dithionate splits up into sulphurous anhydride and manganese sulphate, MnSO_4 . Owing to this, a mixture of manganese sulphate and dithionate is generally obtained in the solution. These may be separated by mixing the solution of the manganese salts with a solution of barium hydroxide, when a precipitate of manganese hydroxide and barium sulphate is obtained. In this manner barium dithionate only is obtained in solution. It is purified by crystallisation, and separates as $\text{BaS}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$; this is then dissolved in water, and decomposed with the requisite amount of sulphuric acid. Dithionic acid, $\text{H}_2\text{S}_2\text{O}_6$, then remains in solution. By concentrating the resultant solution under the receiver of an air-pump it is possible to obtain a liquid of sp. gr. 1.347, but it still contains water, and on further evaporation the acid decomposes into sulphuric acid and sulphurous anhydride: $\text{H}_2\text{S}_2\text{O}_6 = \text{H}_2\text{SO}_4 + \text{SO}_2$. The same decomposition takes place if the solution is slightly heated. Like all the thionic acids, dithionic acid is readily attacked by oxidising agents, and passes into sulphurous acid. No dithionate is able to withstand the action of heat, even though very slight, without giving off sulphurous anhydride: $\text{K}_2\text{S}_2\text{O}_6 = \text{K}_2\text{SO}_4 + \text{SO}_2$. The alkali dithionates have a neutral reaction (which indicates the energetic nature of the acid), are soluble in water, and in this respect present a certain resemblance to the salts of nitric acid (their anhydrides are: N_2O_5 and S_2O_5). Klüss (1888) described many of the salts of dithionic acid.

Langlois, about 1840, obtained a peculiar thionic acid by heating a strong solution of acid potassium sulphite with flowers of sulphur to about 60° , until the disappearance of the yellow coloration first produced by the solution of the sulphur. On cooling, a portion of the sulphur was precipitated, and crystals of a salt of **trithionic acid**, $\text{K}_2\text{S}_3\text{O}_6$ (partly mixed with potassium sulphate), separated out. Plessy afterwards showed that the action of sulphurous acid on a thiosulphate also gives sulphur and trithionic acid: $2\text{K}_2\text{S}_2\text{O}_3 + 3\text{SO}_2 = 2\text{K}_2\text{S}_3\text{O}_6 + \text{S}$. A mixture of potassium acid sulphite and thiosulphate also gives a trithionate. It is very possible that a reaction of the same kind occurs in the formation of trithionic acid by Langlois' method, because potassium sulphite and sulphur yield potassium thiosulphate. The potassium thiosulphate may also be replaced by potassium sulphide, and on passing sulphurous anhydride through the solution, thiosulphate is first formed and then trithionate: $4\text{KHSO}_3 + \text{K}_2\text{S} + 4\text{SO}_2 = 3\text{K}_2\text{S}_3\text{O}_6 + 2\text{H}_2\text{O}$. The sodium salt is not formed under the same circumstances as the corresponding potassium salt. The sodium salt does not crystallise and is very unstable: the barium salt is, however, more stable. The barium and potassium salts are anhydrous: they give neutral solutions and decompose when ignited, with the evolution of sulphur and sulphurous anhydride, a sulphate being left behind, $\text{K}_2\text{S}_3\text{O}_6 = \text{K}_2\text{SO}_4 + \text{SO}_2 + \text{S}$. If a solution of the potassium salt is decomposed by means of hydrofluosilicic or chloric acid, the insoluble salt of the acid used is precipitated and trithionic acid obtained in solution; this acid, however, very easily breaks up on concentration. The addition of salts of copper, mercury, silver, &c., to a solution of a trithionate is followed, either immediately or after a certain time, by the formation of a black precipitate of the sulphides whose formation is due to the decomposition of the trithionic acid with the transference of its sulphur to the metal.

Tetrathionic acid, $\text{H}_2\text{S}_4\text{O}_{10}$, in contradistinction to the preceding acids, is much more stable in the free state than in the form of salts. In the latter form it is easily converted into trithionate, with liberation of sulphur. Sodium tetrathionate was obtained by Fordos and Gélis by the action of iodine on a solution of sodium thiosulphate. The reaction consists essentially in the iodine taking up half the sodium of the thiosulphate. If in the above reaction the sodium thiosulphate be replaced by the lead salt, PbS_2O_3 , the sparingly soluble lead iodide, PbI_2 , and the soluble salt, $\text{PbS}_4\text{O}_{10}$, will be obtained. Moreover the lead salt easily gives tetrathionic acid itself (PbSO_4 is

The compound of sulphur and carbon has been particularly well investigated. It presents a great analogy to carbonic anhydride, in both its

precipitated). The solution of tetrathionic acid may be evaporated over a water-bath, and afterwards in a vacuum, when it gives a colourless liquid, which has no smell and a very acid reaction. When dilute it may be heated to its boiling-point, but in a concentrated form it decomposes into sulphuric acid, sulphurous anhydride, and sulphur: $\text{H}_2\text{S}_4\text{O}_6 = \text{H}_2\text{SO}_4 + \text{SO}_2 + \text{S}_2$.

Pentathionic acid, $\text{H}_2\text{S}_5\text{O}_{11}$, and **hexathionic acid**, $\text{H}_2\text{S}_6\text{O}_{12}$, also belong to this series of acids. But little is known concerning them, either as hydrates or in the form of salts. They are formed, together with other thionic acids, by the direct action of sulphurous acid on sulphuretted hydrogen (in excess) in aqueous solution, a large proportion of sulphur being precipitated at the same time; for instance, $5\text{SO}_2 + 5\text{H}_2\text{S} = \text{H}_2\text{S}_5\text{O}_{11} + 5\text{S} + 4\text{H}_2\text{O}$.

If, as was shown above, the thionic acids are disulphonic acids, they may be obtained, like other sulphonic acids, by means of potassium sulphite and sulphur chloride. Thus, Spring demonstrated the formation of potassium trithionate by the action of sulphur dichloride on a strong solution of potassium sulphite, $2\text{KSO}_3\text{K} + \text{SCl}_2 = \text{S}(\text{SO}_3\text{K})_2 + 2\text{KCl}$. If sulphur chloride is taken, sulphur is also precipitated. The same trithionate is formed by heating a solution of a double thiosulphate, for example, AgKS_2O_3 . Two molecules of the salt then form silver sulphide and potassium trithionate. If the thiosulphate be the potassium silver salt, $\text{SO}_3\text{K}(\text{AgS})$, then the structure of the trithionate must necessarily be $(\text{SO}_3\text{K})_2\text{S}$. Previous to Spring's researches, the action of iodine on sodium thiosulphate was an isolated accidentally discovered reaction; he, however, showed its general significance by testing the action of iodine on mixtures of different sulphur compounds. Thus with iodine, I_2 , the mixture $\text{Na}_2\text{S} + \text{Na}_2\text{SO}_3$ forms $2\text{NaI} + \text{Na}_2\text{S}_2\text{O}_3$, whilst the mixture $\text{Na}_2\text{S}_2\text{O}_3 + \text{Na}_2\text{SO}_3 + \text{I}_2$ gives $2\text{NaI} + \text{Na}_2\text{S}_3\text{O}_6$ —that is, trithionic acid stands in the same relation to thiosulphuric acid as the latter does to sulphuretted hydrogen. And this is the above mode of representation: by replacing one hydrogen in H_2S by sulphoxyl we obtain thiosulphuric acid, HSO_3HS , and by replacing a second hydrogen in the latter again by sulphoxyl we obtain trithionic acid, $(\text{HSO}_3)_2\text{S}$. Furthermore, Spring showed that the action of sodium amalgam on the thionic acids causes reverse reactions to those above indicated for iodine. Thus, sodium thiosulphate with Na_2 gives $\text{Na}_2\text{S} + \text{Na}_2\text{SO}_3$, and Spring showed that the sodium here is not a simple element taking up sulphur, but itself enters into double decomposition, replacing sulphur; for on taking a potassium salt and acting on it with sodium, $\text{KSO}_3(\text{SK}) + \text{NaNa} = \text{KSO}_3\text{Na} + (\text{SK})\text{Na}$. In a similar way sodium dithionate with sodium gives sodium sulphite: $(\text{NaSO}_3)_2 + \text{Na}_2 = 2\text{NaSO}_3\text{Na}$; sodium trithionate forms NaSO_3Na and NaSO_3SNa , and the tetrathionate forms sodium thiosulphate, $(\text{NaSO}_3)_2\text{S}_2(\text{NaSO}_3) + \text{Na}_2 = 2(\text{NaSO}_3)(\text{NaS})$.

In all the oxidised compounds of sulphur we may note the presence of the elements of sulphurous anhydride, SO_2 , the only product of the combustion of sulphur, and in this sense the compounds of sulphur containing one SO_2 are—

$\begin{array}{c} \text{SO}_2\text{H} \\ \text{HO} \end{array}$	$\begin{array}{c} \text{SO}_2\text{HO} \\ \text{HO} \end{array}$	$\begin{array}{c} \text{SO}_2\text{HS} \\ \text{HO} \end{array}$	$\begin{array}{c} \text{SO}_2\text{C}_6\text{H}_5 \\ \text{HO} \end{array}$
Sulphurous acid	Sulphuric acid	Thiosulphuric acid	Benzene sulphonic acid

while, according to this mode of representation, the thionic acids are—

$\begin{array}{c} \text{HO} \\ \text{SO}_2 \end{array}$	$\begin{array}{c} \text{HO} \\ \text{SO}_2 \end{array}$	$\begin{array}{c} \text{HO} \\ \text{SO}_2 \end{array}$	$\begin{array}{c} \text{HO} \\ \text{SO}_2 \end{array}$
SO_2	$\text{SO}_2 \text{ S}$	$\text{SO}_2 \text{ S}_2$	$\text{SO}_2 \text{ S}_3$
SO_2	SO_2	SO_2	SO_2
HO	HO	HO	HO
Dithionic	Trithionic	Tetrathionic	Pentathionic

Hence, it is evident that SO_2 has (whilst CO_2 has not) the faculty for combination, and aims at forming SO_2X_2 , and in general SX_n . To this type, for instance, belong

elementary composition and its chemical character. This substance is the so-called **carbon bisulphide**, CS_2 , and corresponds with CO_2 .

The first endeavours to obtain a compound of sulphur with carbon were unsuccessful, for although sulphur does combine directly with carbon, yet the formation of this compound requires distinctly definite conditions. If sulphur is mixed with charcoal and heated, it is simply driven off from the latter, and not the smallest trace of carbon bisulphide is obtained. The formation of this compound requires that the charcoal should be first heated to a red heat, but not above, and then either the vapour of sulphur passed over it or lumps of sulphur thrown on to the red-hot charcoal, but in small quantities, so as not to lower the temperature of the latter. If the charcoal is heated to a white heat, the amount of carbon bisulphide formed will be less. This depends, in the first place, on the dissociation of the carbon bisulphide at a high temperature.⁶⁹ In the second place, Favre and Silbermann showed that in the combustion of one gram of carbon bisulphide (the products will be $\text{CO}_2 + 2\text{SO}_2$) 3,400 heat units are evolved—that is, the combustion of a molecular quantity of carbon bisulphide evolves 258,400 heat units (according to Berthelot, 246,000). From a molecule of carbon bisulphide in grams we may obtain 12 grams of carbon, whose combustion evolves 96,000 heat units, and 64 grams of sulphur, evolving by combustion (into SO_2) 140,800 heat units. Hence we see that the component elements separately evolve less heat by their combustion (237,000 heat units) than carbon bisulphide itself—that is,

SO_3 , SO_2Cl_2 , $\text{SO}_2\text{Cl}(\text{OH})$, and SF_6 (obtained by Moissan by the action of fluorine on sulphur), but neither SH_2 nor SCl_2 is known. In addition to what has been already said respecting the complex acids formed by sulphur, I think it well to mention that, according to the above view, still more complex oxygen acids and salts of sulphur may be looked for. For instance, the salt $\text{Na}_2\text{S}_4\text{O}_8$ obtained by Villiers (1888) is of this kind. It is formed together with sodium trithionate and sulphur, when SO_2 is passed through a cold solution of $\text{Na}_2\text{S}_2\text{O}_3$, which is then allowed to stand for several days at the ordinary temperature: $2\text{Na}_2\text{S}_2\text{O}_3 + 4\text{SO}_2 = \text{Na}_2\text{S}_4\text{O}_8 + \text{Na}_2\text{S}_3\text{O}_6 + \text{S}$. It may be assumed here, as in the thionic acids, that there are two sulphonyls, bound together not only by S, but also by SO_2 , or, what is almost the same thing, that the sulphonyl is combined with the residue of trithionic acid, i.e., replaces one aqueous residue in trithionic acid.

⁶⁹ Even light decomposes carbon bisulphide, but not to the extent of separating carbon; under the action of the sun's rays it is decomposed into sulphur and a solid substance which is considered to be carbon monosulphide; it is of a red colour, and its sp. gr. is 1.66. (The formation of a red liquid compound, C_3S_2 , has also been remarked.) Thorpe (1889) observed a complete decomposition of carbon bisulphide under the action of a liquid alloy of potassium and sodium; it is accompanied by an explosion and the deposition of carbon and sulphur. A similar complete decomposition of carbon bisulphide is also accomplished by the action of mercury fulminate (Chap. XVI., note 26), and is due to the fact that *at the ordinary temperature* (at which carbon bisulphide is not produced) *the decomposition* of carbon bisulphide takes place with the development of heat—that is, it represents an exothermal reaction, like the decomposition of all explosives.

that heat should be evolved (at the ordinary temperature) and not absorbed in its decomposition, and therefore that the formation of carbon bisulphide from charcoal and sulphur is in all probability accompanied by an absorption of heat.⁷⁰ It is therefore not surprising that, like other compounds produced with an absorption of heat (ozone, nitrous oxide, hydrogen peroxide, &c.), carbon bisulphide is unstable and easily converted into the original substances from which it is obtained. And indeed if the vapour of carbon bisulphide is passed through a red-hot tube, it is decomposed—that is, it dissociates—into sulphur and carbon. And this takes place at the temperature at which this substance is formed, just as water decomposes into hydrogen and oxygen at the temperature of its formation. By this absorption of heat in the formation of carbon bisulphide is explained the facility with which it suffers reactions of decomposition, which we shall see in the sequel. and its main difference from the closely analogous carbonic anhydride.

In the laboratory carbon bisulphide is prepared as follows: A porcelain tube is luted into a furnace in an inclined position, the upper extremity of the tube being closed by a cork, and the lower end connected with a condenser. The tube contains charcoal, which is raised to a red heat, and pieces of sulphur are then placed in the upper end. The sulphur melts, and its vapour comes into contact with the red-hot charcoal, when combination takes place; the vapours condense in a well-cooled condenser, carbon bisulphide being a liquid boiling at 48°. On a large scale the apparatus depicted in fig. 101 is employed. A cast-iron cylinder rests on a stand in a furnace. Wood charcoal is charged into the cylinder through the upper tube closed by a clay stopper, while the sulphur is introduced through a tube reaching to the bottom of the cylinder. Pieces of sulphur thrown into this tube

⁷⁰ The fact should not be lost sight of that sulphur and charcoal are solids at the ordinary temperature, whilst carbon bisulphide is a very volatile liquid, and consequently, in the act of combination, referred to the ordinary temperature, there is, as it were, a passage into a liquid state, and this requires the absorption of heat. And, furthermore, the molecule of sulphur contains at least six atoms, and the molecule of carbon in all probability (Chap. VIII.) a very considerable number of atoms; thus, the action of sulphur on charcoal may be expressed in the following manner: $3C_n + nS_6 = 3nCS_2$; that is, from $n+3$ molecules there proceed $3n$ molecules, and as n must be very considerable, $3n$ must be greater than $3+n$, which indicates a decomposition in the formation of carbon bisulphide, although the reaction at first sight appears as one of combination. This decomposition is seen also from the volumes in the solid and liquid states. Carbon bisulphide has a sp. gr. of 1.29; hence its molecular volume is 59. But the volume of carbon, even in the form of charcoal, is not more than 6, and the volume of S_2 is 30; hence 36 volumes after combination give 59 volumes—an expansion takes place, as in decompositions. The physical work of converting the solids (sulphur and carbon) into a liquid, the mechanical work of increasing the volume, and the chemical work of depolymerisation of the carbon and sulphur naturally require much heat. This example illustrates the complexity of thermo-chemical phenomena.

fall on to the bottom of the cylinder, and are converted into vapour, which passes through the entire layer of charcoal in the cylinder. The vapour of carbon bisulphide thus formed passes through the exit tube, first into a Woulfe's bottle (where the sulphur which has not entered into the reaction is condensed), and then into a strongly cooled condenser or worm.⁷¹

Pure carbon bisulphide is a colourless liquid, which refracts light strongly, and has a pure ethereal smell ; at 0° its specific gravity is 1.293, and at 15°, 1.271. If kept for a long time it seems to undergo a change, especially when it is kept under water, in which it is insoluble. It boils at 48°, and the pressure of its vapour is so great that it evaporates

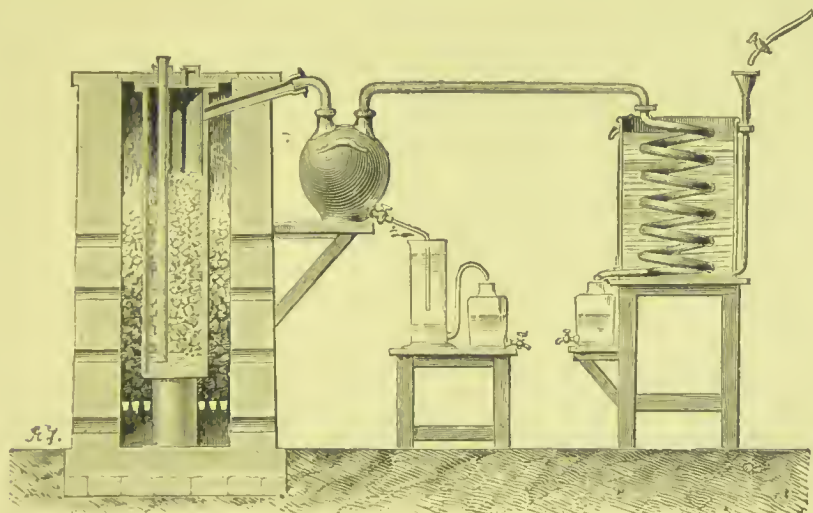


FIG. 101.—Apparatus for the manufacture of carbon bisulphide.

very easily, producing cold,⁷² and therefore it has to be kept in well-stoppered vessels ; it is generally kept under a layer of water, which hinders its evaporation and does not dissolve it.⁷³

⁷¹ Carbon bisulphide, as prepared on a large scale, is generally very impure, and contains not only sulphur, but, more especially, other impurities which give it a very disagreeable odour. The best method of purifying this malodorous carbon bisulphide is to shake it up with a certain amount of mercuric chloride, or even simply with mercury, until the surface of the metal ceases to turn black. After this the carbon bisulphide must be poured off and distilled over a water-bath, after mixing with some oil to retain the impurities.

⁷² If carbon bisulphide be evaporated under the receiver of an air-pump, or by means of a current of air, it is possible to obtain a temperature as low as -60° , and the carbon bisulphide does not solidify at this temperature. However, if a series of air-bubbles is passed through it by means of bellows, a crystalline white substance remains which volatilises below 0°: this is a hydrate, $\text{H}_2\text{O}, 2\text{CS}_2$, which easily decomposes into water and carbon bisulphide. It is formed in the above experiment by the moisture held in the air passed through the carbon bisulphide, and by the fall of temperature.

⁷³ Strong alcohol is miscible in all proportions with carbon bisulphide, but dilute alcohol only in a definite amount, owing to its diminished solubility from the presence of the water in it. Ether, hydrocarbons, fatty oils, and many other organic substances are

Carbon bisulphide enters into many combinations, which are frequently closely analogous to the compounds of carbonic anhydride. In this respect it is a **thio-anhydride**—i.e., it has the character of the acid anhydrides,^{73a} like carbonic anhydride, with the difference that the oxygen of the latter is replaced by sulphur. By thio-compounds are understood, in general, those compounds of sulphur which correspond with the oxygen compounds, but with substitution of sulphur for oxygen. Thus, thiosulphuric acid is mono-thiosulphuric acid—that is, sulphuric acid in which one atom of sulphur replaces one atom of oxygen. With the sulphides of the alkalis and alkaline earths, it forms saline substances corresponding with the carbonates, and these compounds may be termed **thio-carbonates**. For example, the composition of the sodium salt, Na_2CS_3 , is exactly like that of sodium carbonate. These salts are formed by the direct solution of carbon bisulphide in aqueous solutions of the sulphides; but they are difficult to obtain in a crystalline form, because they are easily decomposable. When their solutions are highly concentrated they begin to decompose, with the evolution of sulphuretted hydrogen and the formation of a carbonate, water taking part in the reaction—for example, $\text{K}_2\text{CS}_3 + 3\text{H}_2\text{O} = \text{K}_2\text{CO}_3 + 3\text{H}_2\text{S}$.⁷⁴

soluble with great ease in carbon bisulphide. This is taken advantage of in practice for extracting the fatty oils from vegetable seeds, such as linseed, palm-nuts, or from bones, &c. The preparation of vegetable oils is usually carried out by pressing the seeds under a press, but the residue always contains a certain amount of oil. These traces of oil can, however, be removed by treatment with carbon bisulphide. In this manner a solution is obtained which when heated readily parts with all the carbon bisulphide, leaving the non-volatile fatty oil behind, so that the same carbon bisulphide may be condensed and used over again for the same purpose. It also dissolves iodine, bromine, indiarubber, sulphur, and certain resins.

Carbon bisulphide, especially at high temperatures, very often acts by its elements in a manner in which carbon and sulphur alone are not able to react, which will be understood from what has been said above respecting its endothermal origin. If it is passed over red-hot metals—over copper, for instance, not to mention sodium, &c.—it forms a sulphide of the metal and deposits charcoal, and if the vapour is passed over incandescent metallic oxides it forms metallic sulphides and carbonic anhydride (and sometimes a certain amount of sulphurous anhydride). Lime and similar oxides give under these circumstances a carbonate and a sulphide—for example, $\text{CS}_2 + 3\text{CaO} = 2\text{CaS} + \text{CaCO}_3$. The sulphides obtained by this means are often well crystallised, like those found in nature—for example, lead and antimony sulphides.

^{73a} And just as COCl_2 corresponds to CO_2 , so also the chloranhydride, CSCl_2 , or *thiophosgene*, corresponds to CS_2 .

⁷⁴ If instead of a sulphide we take an alkali hydroxide, a thiocarbonate is also formed, together with a carbonate—thus, $3\text{BaH}_2\text{O}_2 + 3\text{CS}_2 = 2\text{BaCS}_3 + \text{BaCO}_3 + 3\text{H}_2\text{O}$. From the instability of the thiocarbonates of the alkaline metals we can clearly see the reason of the difficulty with which the salts of the heavier metals are formed, whose basic properties are incomparably weaker. However, these salts may be obtained by double decomposition. The potassium salt, K_2CS_3 , is employed in vineyards as a preventive of phylloxera.

Carbon bisulphide forms compounds not only with the metallic sulphides, but also

A remarkable example ^{74a} of the thio-compounds is found in **thio-cyanic acid**—i.e., cyanic acid in which the oxygen is replaced by sulphur, HCNS. We know (Chap. IX.) that with oxygen the cyanides of the alkaline metals, RCN, give cyanates, RCNO; but they also combine with sulphur, and therefore if yellow prussiate of potash be treated as in the preparation of potassium cyanide, and sulphur be added to the mass, **potassium thiocyanate**, KNCS, will be obtained in solution. This salt is much more stable than potassium cyanate; it dissolves without change in water and alcohol, forming colourless solutions from which it easily crystallises on evaporation; it may be kept exposed to air even when in solution. In dissolving in water it absorbs a considerable amount of heat, and forms the starting-point for the preparation of all the thiocyanates, RCNS, and organic compounds in which the metals are replaced by hydrocarbon groups. Such, for example, is volatile mustard oil, C_3H_5CSN (allyl thiocyanate),⁷⁵ which gives to mustard its caustic properties. With ferric salts the thiocyanates give an exceedingly brilliant red coloration, which serves for

with sulphuretted hydrogen—that is, it forms **thiocarbonic acid**, H_2CS_3 . This is obtained by carefully mixing solutions of thiocarbonates with dilute hydrochloric acid, and separates in an oily layer, which easily decomposes in the presence of water into sulphuretted hydrogen and carbon bisulphide, just as the corresponding carbonic acid (hydrate) decomposes into water and carbonic anhydride. Carbon bisulphide combines not only with sodium sulphide, but also with the bisulphide, Na_2S_2 , not, however, with the trisulphide, Na_2S_3 . Organic compounds, like alcohol, C_2H_5OH or $EtOH$, when treated with caustic alkalis and CS_2 give xanthates, $(EtO)(MS)CS$, which are yellow and easily decompose. Cellulose, $C_6H_{10}O_5$, has the faculty of entering into a similar form of reaction, in the state of fibre or otherwise. When treated with a solution of $NaHO$ it forms a sodium derivative (part of the H in OH is replaced by Na), and this, with CS_2 , forms a xanthic compound which is reconverted into cellulose by the action of acids. This reconverted cellulose has the appearance of a viscid gelatinous mass known as **viscose**, which can be drawn into threads, formed into films, and used to attach (glue) objects together. After drying, there remains cellulose, for instance in the form of fibre, having a silky lustre, transparent and elastic, &c. This discovery of Cross and Bevan (1896) may find many most useful applications, and is already employed for the manufacture of artificial silk.

^{74a} The relation of carbon bisulphide to the carbon compounds presents many other most interesting features which are considered in organic chemistry. We will here turn our attention to organic sulphides. Ethyl sulphide, $(C_2H_5)_2S$, combines with ethyl iodide, C_2H_5I , forming a molecule, $S(C_2H_5)_3I$. This compound is of a saline character, corresponds with salts of the alkalies, and is closely analogous to ammonium chloride. It is soluble in water; when heated, it again splits up into its components EtI and Et_2S , and with silver hydroxide gives a hydroxide, $Et_3S \cdot OH$, having the property of a distinct and energetic alkali, resembling caustic ammonia. Hence, sulphur here enters into a relation towards other elements similar to that of nitrogen in ammonia and ammonium salts. Judging from the existence of the ethyl-sulphine compounds, it might be imagined that sulphur forms a compound, SH_4 , with hydrogen; but no such compound is known, just as NH_5 is unknown, although NH_4Cl exists.

⁷⁵ Although mustard oil may be obtained from the thiocyanates, it is only an isomeride of allyl thiocyanate proper, as is explained in organic chemistry.

detecting the smallest traces of ferric salts in solution. Thiocyanic acid, HCNS , may be obtained by a method of double decomposition, by distilling potassium thiocyanate with dilute sulphuric acid. It is a volatile colourless liquid, having a smell recalling that of vinegar, is soluble in water, and may be kept in solution without change.^{75a} The thiocyanates are fully described in works on organic chemistry.

The sulphur compounds of chlorine, Cl_2S and Cl_2S_2 , may be regarded as products, on the one hand, of the metalepsis of H_2S and H_2S_2 , and, on the other hand, of the oxygen compounds of chlorine, because chloride of sulphur, Cl_2S , resembles chlorine oxide, Cl_2O ; or, thirdly, we may see in these compounds the type of the acid chloranhydrides, because they are all decomposed by water, forming hydrochloric acid, and sulphur tetrachloride, SCl_4 , corresponds to SO_2 just as PCl_3 does to P_2O_3 , and forms HCl and SO_2 with water.⁷⁶

The compounds of sulphur with chlorine are prepared in the apparatus depicted in fig. 102. As sulphur chloride is decomposed by water, the chlorine evolved in the flask C must be dried before coming into contact with the sulphur. It is therefore passed first through a Woulfe's bottle, B, containing sulphuric acid, and then through the

^{75a} Sulphur can only replace half the oxygen in CO_2 , as is seen in carbon oxysulphide, or monothiocarbonic anhydride, COS . This substance was obtained by Than, and is formed in many reactions. A certain amount is obtained if a mixture of carbonic oxide and the vapour of sulphur is passed through a red-hot tube. When carbon tetrachloride is heated with sulphurous anhydride, this substance is also formed; but it is best obtained in a pure form by decomposing potassium thiocyanate with a mixture of equal volumes of water and sulphuric acid. A gas is then evolved containing a certain amount of hydrocyanic acid, from which it may be freed by passing it over wool containing moistened mercuric oxide, which retains the hydrocyanic acid. The reaction is expressed by the equation: $2\text{KCNS} + 2\text{H}_2\text{SO}_4 + 2\text{H}_2\text{O} = \text{K}_2\text{SO}_4 + (\text{NH}_4)_2\text{SO}_4 + 2\text{COS}$. It is also formed by passing the vapour of carbon bisulphide over alumina or clay heated to redness (Gautier; silicon sulphide is then formed). COS is also formed by passing phosgene over a long layer of asbestos mixed with sodium sulphide at 270° ; $\text{CdS} + \text{COCl}_2 = \text{CdCl}_2 + \text{COS}$ (Nuricsán, 1892). The pure gas has an aromatic odour, is soluble in its own volume of water, which, however, acts on it, so that it must be collected over mercury. When slightly heated, carbon oxysulphide decomposes into sulphur and carbonic oxide. It burns in air with a pale blue flame, explodes with oxygen, and yields potassium sulphide and carbonate with potassium hydroxide: $\text{COS} + 4\text{KHO} = \text{K}_2\text{CO}_3 + \text{K}_2\text{S} + 2\text{H}_2\text{O}$.

⁷⁶ There is no reason for seeing any contradiction or mutual incompatibility in these three views, because every analogy is more or less modified by a change of elements. Thus, for instance, it cannot be expected that the product of the metalepsis of hydrogen sulphide would resemble the corresponding products of water in all respects, because water has not the acid properties of hydrogen sulphide. In the days of dualism and electrical polarity it was supposed that the sulphur varied in its nature: in hydrogen sulphide or potassium sulphide it was considered to be negative, and in sulphurous anhydride or sulphur dichloride, positive. This differs but little from the view held by those who consider that sulphur is divalent in some compounds (H_2S , SCl_2), tetravalent in others (SO_2 , SCl_4 , SEt_3T), and hexavalent in others (SO_3 , SF_6), and that it is different in each of these states.

cylinder D containing pumice-stone moistened with sulphuric acid, and is then led into the retort E, in which the sulphur is heated. The compound which is formed distils over into the receiver R. A certain amount of sulphur passes over with the sulphur chloride, but if the resultant distillate is re-saturated with chlorine and distilled no free sulphur remains, the boiling-point rises to 144° , and pure **sulphur chloride**, S_2Cl_2 , is obtained. Its formula is doubled because its vapour density referred to hydrogen is 68. It is also obtained by heating certain metallic chlorides (stannous, mercuric) with sulphur; both the metal and chlorine then combine with the sulphur. Sulphur chloride is a yellowish-brown liquid, which boils at 144° , and has a specific gravity of 1.70 at 0° . It fumes strongly in the air, reacting on

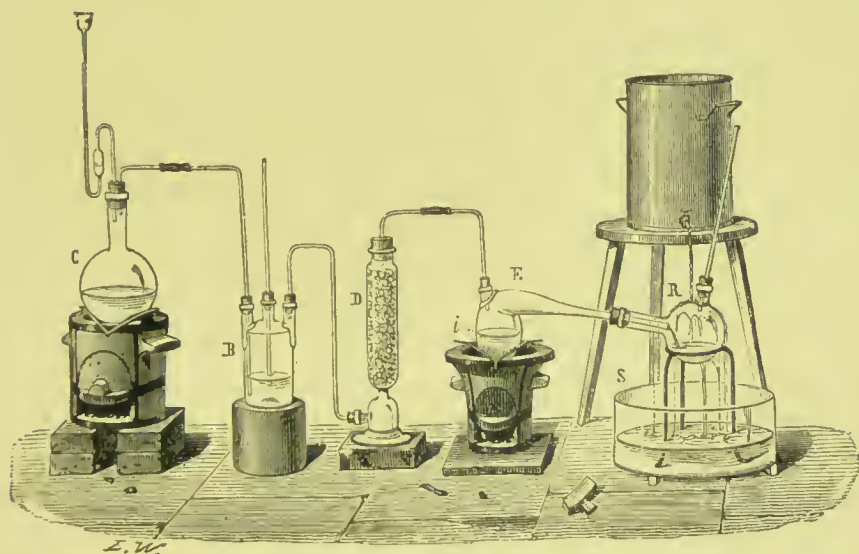


FIG. 102.—Apparatus for the preparation of sulphur chloride, and similar volatile compounds prepared by combustion in a stream of chlorine.

the moisture contained therein, and has a heavy chloranhydrous odour. It dissolves sulphur, is miscible with carbon bisulphide, and falls to the bottom of a vessel containing water, by which it is decomposed, forming sulphurous anhydride and hydrochloric acid; but it first forms various lower stages of oxidation of sulphur, because the addition of silver nitrate to the solution gives a black precipitate. With hydrogen sulphide it gives sulphur and hydrochloric acid, and it reacts directly with metals—especially arsenic, antimony, and tin—forming sulphides and chlorides. In the cold, it absorbs chlorine and gives **sulphur dichloride**, SCl_2 . The entire conversion into this substance requires the prolonged passage of dry chlorine through sulphur chloride surrounded by a freezing mixture. The distillation of the dichloride must be conducted in a stream of chlorine, as otherwise it partially

decomposes into sulphur chloride and chlorine. Pure sulphur dichloride is a reddish-brown liquid, which resembles the lower chloride in many respects; its specific gravity is 1.62; its odour is more suffocating than that of sulphur chloride; it volatilises at 64° .⁷⁷

Thionyl chloride, SOCl_2 , may be regarded as oxidised sulphur dichloride; it corresponds with sulphur chloride, S_2Cl_2 , in which one atom of sulphur is replaced by oxygen. At the same time it is chlorine oxide (hypochlorous anhydride, Cl_2O) combined with sulphur, and also the chloranhydride of sulphurous acid—that is, $\text{SO}(\text{HO})_2$, in which the two hydroxyl groups are replaced by two atoms of chlorine, or sulphurous anhydride, SO_2 , in which one atom of oxygen is replaced by two atoms of chlorine. All these representations are confirmed by reactions of formation or decomposition; they all agree with our notions of the other compounds of sulphur, oxygen, and chlorine. Thionyl chloride was first obtained by Schiff by the action of dry sulphurous anhydride on phosphorus pentachloride. On distilling the resultant liquid, thionyl chloride comes over first at 80° , and on continuing the distillation phosphorus oxychloride distils over at above 100° , $\text{PCl}_5 + \text{SO}_2 = \text{POCl}_3 + \text{SOCl}_2$. This mode of preparation is direct evidence of the oxychloride character of SOCl_2 . Würtz obtained the same substance by passing a stream of chlorine oxide through a cold solution of sulphur in sulphur chloride; the chlorine oxide then combined directly with the sulphur, $\text{S} + \text{Cl}_2\text{O} = \text{SOCl}_2$, whilst the sulphur chloride remained unchanged (sulphur explodes with chlorine oxide). Thionyl chloride is a colourless liquid, with a suffocating acrid smell; it has a specific gravity at 0° of 1.675, and boils at 78° . It sinks in water, by which it is immediately decomposed, like all chloranhydrides—for example, like

⁷⁷ The observed vapour density of sulphur dichloride referred to hydrogen is 53.3, and that given by the formula, 51.5. The smaller molecular weight explains its boiling-point being lower than that of sulphur chloride, S_2Cl_2 . The reactions of these two compounds are very similar. Sulphur converts the dichloride, S_2Cl_2 , into the monochloride, S_2Cl_2 . In one point the dichloride differs distinctly from the monochloride—that is, in its capacity for easily giving up chlorine and decomposing. Even light decomposes it into chlorine and the monochloride. Hence it acts on many substances in the same manner as chlorine, or substances which easily part with the latter, such as phosphoric or anti-monic chloride. In distinction from these, however, sulphur dichloride would appear to distil without any considerable decomposition, judging by the vapour density. But this is not a valid conclusion, for if there be a decomposition, then $2\text{S}_2\text{Cl}_2 = \text{S}_2\text{Cl}_2 + \text{Cl}_2$; now the density of sulphur chloride is 67.5, and that of chlorine, 35.5, and consequently a mixture of equal volumes of the two would give 51.5, just the same as sulphur dichloride. *Therefore the distillation of sulphur dichloride is probably nothing but its decomposition*, and it must then be admitted that the compound S_2Cl_2 , which is stable at the ordinary temperature, decomposes at 64° . On cooling to -25° it absorbs a further amount of chlorine, corresponding to S_2Cl_4 , but even at -10° a portion of the absorbed chlorine is given off—that is, dissociation takes place. Thus the tetrachloride is even less stable than the dichloride. S_2Cl_2 and S_2Cl_4 are able to combine with SnCl_4 , AsCl_3 , &c., forming solid crystalline substances.

carbonyl chloride, which corresponds with it: $\text{SOCl}_2 + \text{H}_2\text{O} = \text{SO}_2 + 2\text{HCl}$.^{77a}

Normal sulphuric acid has two corresponding chloranhydrides; the first, $\text{SO}_2(\text{OH})\text{Cl}$, is sulphuric acid, $\text{SO}_2(\text{HO})_2$ in which one equivalent of HO is replaced by chlorine; the second has the composition SO_2Cl_2 —that is, two HO groups are substituted by two of chlorine. It is called **sulphuryl chloride**, and the first chloranhydride, SO_2HOCl , may be called chlorosulphonic acid, because it retains one hydroxyl of sulphuric acid, and its corresponding salts are known. Thus, potassium chloride absorbs the vapour of sulphuric anhydride, forming a salt, SO_3KCl , corresponding with SO_3HCl as acid. This first chloranhydride of sulphuric acid, SO_2HOCl , discovered by Williamson, is obtained either by the action of phosphorus pentachloride (or even POCl_3) on sulphuric acid ($\text{PCl}_5 + \text{H}_2\text{SO}_4 = \text{POCl}_3 + \text{HCl} + \text{HSO}_3\text{Cl}$), or directly by the action of dry hydrochloric acid on sulphuric anhydride, $\text{SO}_3 + \text{HCl} = \text{HSO}_3\text{Cl}$. The most easy and rapid method of its formation is by direct saturation of cold Nordhausen acid with dry hydrochloric acid gas ($\text{SO}_3 + \text{HCl} = \text{HSO}_3\text{Cl}$), and distillation of the resultant solution; the distillate then contains HSO_3Cl . It is a colourless fuming liquid, having an acrid odour; it boils at 153° (according to my determination, confirmed by Konovaloff), and its specific gravity at 19° is 1.776. It is immediately decomposed by water, forming hydrochloric and sulphuric acids, as should be the case with a true chloranhydride. In the reactions of this chloranhydride we find the easiest means of introducing the sulphonic group HSO_3 into other compounds, because it is here combined with chlorine. **Sulphuryl chloride**, SO_2Cl_2 , was obtained by Regnault by the direct action of the sun's ray (or in the presence of acetic acid or carbon, or, better still, in the presence of camphor) on a mixture of equal volumes of chlorine and sulphurous oxide. The gases gradually condense into a liquid, combining together as carbonic oxide does with chlorine. The first chloranhydride, SO_3HCl , decomposes, when heated at 200° in a closed tube, into sulphuric acid and sulphuryl chloride. It boils at 76° , its specific gravity is 1.70, it gives hydrochloric and sulphuric acids^{77b} with water, fumes in the air,

^{77a} Hartog and Sims (1893) obtained thionyl bromide, SOBr_2 , by treating SOCl_2 with sodium bromide; it is a red liquid of sp. gr. 2.62, and decomposes at 150° . Thorpe and Rodger (1889), by heating a mixture of lead fluoride and phosphorus pentasulphide to 250° in an atmosphere of dry nitrogen, obtained gaseous **phosphorus fluosulphide** or thiophosphoryl fluoride, PSF_3 , corresponding with POCl_3 . This colourless gas is converted into a colourless liquid by a pressure of 11 atmospheres; it does not act upon dry mercury and takes fire spontaneously in air or oxygen, forming phosphorus pentafluoride, phosphorous anhydride, and sulphurous anhydride.

^{77b} Baeyer and Villiger obtained a crystalline compound, SO_2Cl_2 , with water in the cold. It is an interesting but little-known compound.

and, judging by its vapour density, does not decompose when distilled.⁷⁸

Moissan and Lebeau (1900) obtained **hexafluoride of sulphur**, SF_6 , by the direct action of free fluorine on sulphur (absorbing the foreign gases in KHO). It crystallises at -55° , has no smell or taste, and is only slightly soluble in water. Its density compared with that of hydrogen is 72 (according to its formula, 63.5). It is not acted on by alkalis, even with the aid of heat, and is almost as inactive as nitrogen. However, if this gas is mixed with hydrogen and a series of electric sparks passed through the mixture, it is decomposed with the formation of HF, H_2S , sulphur, &c. The formation of this remarkable substance clearly shows the power of sulphur to give, like the elements of group VI., compounds of the type SX_6 , an instance of which is seen in sulphuric acid itself, $\text{SO}_2(\text{OH})_2$.^{78a}

⁷⁸ Pyrosulphuryl chloride, $\text{S}_2\text{O}_5\text{Cl}_2$. See note 44. Thorpe and Kirman, by treating SO_3 with HF, obtained $\text{SO}_2(\text{OH})\text{F}$, as a liquid boiling at 163° , but which decomposed with great facility and then gave SO_2F_2 .

^{78a} The acids of sulphur naturally have their corresponding ammonium salts, and the latter their amides and nitriles. It will be readily understood how vast a field for research is presented by the series of compounds of sulphur and nitrogen, if we only remember that, as we saw in Chap. IX., there is a vast series of derivatives corresponding with the ammonium salts of carbonic and formic acids. To sulphuric acid there correspond: two ammonium salts, $\text{SO}_2(\text{HO})(\text{NH}_4\text{O})$ and $\text{SO}_2(\text{NH}_4\text{O})_2$; three amides—the acid amide, $\text{SO}_2(\text{HO})(\text{NH}_2)$, or sulphamic acid, the normal saline compound $\text{SO}_2(\text{NH}_4\text{O})(\text{NH}_2)$, or ammonium sulphamate, and the normal amide $\text{SO}_2(\text{NH}_2)_2$, or sulphamide (the analogue of urea); then the acid nitrile, $\text{SON}(\text{HO})$, and two neutral nitriles, $\text{SON}(\text{NH}_2)$ and SN_2 . There are similar compounds corresponding with sulphurous acid, and therefore its nitriles will be, an acid, $\text{SN}(\text{HO})$, its salt and the normal compound, $\text{SN}(\text{NH}_2)$. Dithionic and the other acids of sulphur should also have their corresponding amides and nitriles. Only a few examples are known, which we shall briefly describe. Sulphuric acid forms salts of very great stability with ammonia, and ammonium sulphate is one of the commonest ammoniacal compounds. It is obtained by the direct action of ammonia on sulphuric acid, or by the action of the latter on ammonium carbonate; it separates from its solutions in an anhydrous state, like potassium sulphate, with which it is isomorphous. Hence the composition of the crystals of **ammonium sulphate** is $(\text{NH}_4)_2\text{SO}_4$. This salt fuses at 140° , and does not undergo any change when heated up to 180° . At higher temperatures it does not lose water, but parts with half its ammonia, and is converted into the acid salt, HNH_4SO_4 ; and this acid salt, on further heating, undergoes a further decomposition, and splits up into nitrogen, water, and acid ammonium sulphite, HNH_3SO_3 . At the ordinary temperature the normal salt is soluble in twice its weight of water and at the boiling-point of water in an equal weight. In its faculty for combination this salt exhibits a great resemblance to potassium sulphate, and, like it, easily forms a number of double salts, the most remarkable of which are the ammonia alums, $\text{NH}_4\text{AlS}_2\text{O}_8 \cdot 12\text{H}_2\text{O}$, and the double salts formed by the metals of the magnesium group, having, for example, the composition $(\text{NH}_4)_2\text{MgS}_2\text{O}_8 \cdot 6\text{H}_2\text{O}$. Ammonium sulphate does not give an amide when heated, perhaps owing to the power of sulphuric anhydride of retaining the water combined with it with great force. But the amides of sulphuric acid may be very conveniently prepared from sulphuric anhydride. Their formation by this method is very easily understood, because an anide is equal to an ammonium salt less water, and if the anhydride be taken it will give an amide directly with ammonia. Thus, if dry ammonia is passed into

In the group of the halogens we saw four closely analogous elements—fluorine, chlorine, bromine, and iodine—and we meet with the same

a vessel surrounded by a freezing mixture and containing sulphuric anhydride, it forms a white powdery mass called **sulphatammon**, having the composition $\text{SO}_3, 2\text{H}_3\text{N}$ and resembling the similar compound of carbonic acid, $\text{CO}_2, 2\text{NH}_3$. This substance is naturally the ammonium salt of sulphamic acid, $\text{SO}_2(\text{NH}_4\text{O})\text{NH}_2$. It is slowly acted on by water, and may therefore be obtained in solution, in which it slowly reacts with barium chloride, which proves that with water it still forms ammonium sulphate. If this substance is carefully dissolved in water and evaporated, it yields well-formed crystals, whose solution no longer gives a precipitate with barium chloride. This is due to a change in the nature of the substance, and therefore Rose calls the crystalline modification **parasulphatammon**. Platinum chloride only precipitates half the nitrogen as platinochloride from solutions of sulphat- and parasulphat-ammon, which shows that they are ammonium salts, $\text{SO}_2(\text{NH}_4\text{O})(\text{NH}_2)$. It may be that the reason of the difference in the two modifications is connected with the fact that two different substances of the composition $\text{N}_2\text{H}_4\text{SO}_2$ are possible: one is the amide $\text{SO}_2(\text{NH}_2)_2$, corresponding with the normal salt, and the other is the salt of the nitrile acid, corresponding with acid ammonium sulphate—that is, $\text{SON}(\text{ONH}_4)$ corresponds with the acid $\text{SON}(\text{OH}) = \text{SO}_2(\text{NH}_4\text{O})\text{OH} - 2\text{H}_2\text{O}$. Hence, there may here be a difference of the same nature as that between urea and ammonium cyanate. Up to the present, the isomerism indicated above has been but little investigated, and might be the subject of interesting researches.

If in the preceding experiment the ammonia, and not the sulphuric anhydride, is taken in excess, a soluble substance of the composition $2\text{SO}_3, 3\text{NH}_3$ is formed. This compound, obtained by Jacqueline and investigated by Voronin, doubtless also contains a salt of sulphamic acid—that is, of the amide corresponding with the acid ammonium sulphate = $\text{HNH}_4\text{SO}_4 - \text{H}_2\text{O} = (\text{NH}_3)\text{SO}_2(\text{OH})$. Probably it is a compound of sulphatammon with sulphamic acid. Thus it has an acid reaction, and does not give a precipitate with barium chloride.

With normal sulphate of ammonium, an amide of the composition $\text{N}_2\text{H}_4\text{SO}_2$ should correspond, which should bear the same relation to sulphuric acid as urea bears to carbonic acid. This amide, known as **sulphamide**, is obtained by the action of dry ammonia on the sulphuryl chloride, SO_2Cl_2 : $\text{SO}_2\text{Cl}_2 + 4\text{NH}_3 = \text{N}_2\text{H}_4\text{SO}_2 + 2\text{NH}_4\text{Cl}$, just as urea is obtained by the action of ammonia on carbonyl chloride. The ammonium chloride is separated from the resultant sulphamide with great difficulty. Cold water, acting on the mixture, dissolves them both; the cold solution does not give a precipitate with barium chloride. Alkalies act on it slowly, as they do on urea; but on boiling, especially in the presence of alkalies or acids, it easily re-combines with water, and gives an ammonium salt. V. Traube (1892) obtained sulphamide by the reaction of sulphuryl chloride dissolved in chloroform upon ammonia. The resultant precipitate dissolves when shaken up with water, and the solution (after boiling with the oxides of lead or silver) is evaporated, when a syrupy liquid remains. With nitrate of silver the latter gives a solid compound, which, when decomposed by hydrochloric acid, gives free sulphamide in large colourless crystals, having the composition $\text{SO}_2(\text{NH}_2)_2$. This substance fuses at 81° , begins to decompose below 100° , and is entirely decomposed above 250° ; it is soluble in water, and the solution has a neutral reaction and bitter taste. When heated with acids, sulphamide gradually decomposes, forming sulphuric acid and ammonia. If the silver compound obtained by the action of sulphamide on nitrate of silver is heated at 170° – 180° until ammonia is no longer evolved, and the residue extracted with water acidulated with nitric acid, a salt separates out from the solution, answering in its composition to sulphamide, SO_2NAg , which = the amide – $\text{NH}_3 = \text{SO}_2\text{N}_2\text{H}_4 - \text{NH}_3 = \text{SO}_2\text{NH}$. The action of sulphuryl chloride (and of the other chloranhydrides of sulphur) on ammonium carbonate always, as Mente showed (1888), results in the formation of the salt $\text{NH}(\text{SO}_3\text{NH}_4)_2$.

The nitriles corresponding with sulphuric acid are not as yet known with any

number of closely allied analogues in the oxygen group; for besides sulphur this group also includes **selenium** and **tellurium**: O, S, Se, Te. These two groups are very closely allied, both in respect to the magnitudes of their atomic weights and also in the faculty of the elements of both groups for combining with metals. The distinct analogy and definite degree of variance known to us for the halogens also repeat themselves in the same degree for the elements of the oxygen group. Amongst the halogens, fluorine has many peculiarities compared with Cl, Br, and I, which are more closely analogous, whilst oxygen differs in many respects from S, Se, Te, which possess greater similarities. The analogy in a quantitative respect is perfect in both cases. Thus the halogens combine with H, and the elements of the oxygen group with

certainly. The most simple nitrile corresponding with sulphuric acid should have the composition $\text{N}_2\text{H}_3\text{SO}_4 - 4\text{H}_2\text{O} = \text{N}_2\text{S}$. This would be a kind of cyanogen corresponding with sulphuric acid. On comparing sulphurous acid with carbonic acid we saw that they present a great analogy in many respects, and therefore it might be expected that nitrile compounds having the composition NHS and N_2S_2 would be found. The latter of these compounds is well known, and was obtained by Soubeiran by the action of dry ammonia on sulphur chloride dissolved in benzene. This substance corresponds with cyanogen (paracyanogen), and is known as **nitrogen sulphide**. It is formed according to the equation: $3\text{SCl}_2 + 8\text{NH}_3 = \text{N}_2\text{S}_2 + \text{S} + 6\text{NH}_4\text{Cl}$. The free sulphur and nitrogen sulphide are dissolved by acting on the product with carbon bisulphide, the nitrogen sulphide being much less soluble than the sulphur. It is a yellow substance, which is excessively irritating to the eyes and nostrils. It explodes when rubbed with a hard substance, being naturally decomposed with the evolution of nitrogen; but when heated it fuses without decomposing, and only decomposes with explosion at 157° . It is insoluble in water, and only slightly so in alcohol, ether, and carbon bisulphide; 100 parts of the latter dissolve 1.5 part of nitrogen sulphide at the boiling-point. This solution on cooling deposits the sulphide in minute transparent prisms of a golden yellow colour.

A mixture of S_4N_4 and chloroform gives a precipitate of $\text{S}_4\text{N}_4\text{Cl}_4$ when treated with chlorine (Demarçay, Muthmann, and others), and $\text{S}_4\text{N}_3\text{Cl}$ when treated with a chloroform solution of S_2Cl_2 . The latter compound has the appearance of golden scales which dissolve in water with difficulty, but are soluble in strong nitric acid, forming, when evaporated *in vacuo*, an explosive substitution product, $\text{S}_4\text{N}_3\text{NO}_3$, as large yellow crystals which are soluble in water, but readily decompose. In general Muthmann and Scitter (1897) obtained a series of compounds, $\text{S}_4\text{N}_3\text{X}$, apparently of a saline character. Their relation to other compounds of S and N cannot yet be regarded as clear. If a solution of $\text{S}_4\text{N}_3\text{Cl}$ in methyl alcohol is treated (until it turns red) with zinc dust, it (Muthmann and Clever, 1896) forms **nitrogen pentasulphide**, N_2S_5 (in some respects the analogue of N_2O_5), which is a remarkable substance in many ways, although not evincing the character of a thio-acid anhydride with any clearness. It is obtained by heating a solution of three parts of S_4N_4 in fifty parts of CS_2 in a closed vessel (five atmospheres pressure) at 100° for some time. On evaporating the filtrate it deposits sulphur and a dark-red strongly smelling oil, which is purified by dissolving it in ether and, when pure, fuses at about 10° and resembles iodine in its appearance. It decomposes when heated, forms NH_3 with water, and is apparently formed together with free cyanogen sulphide: $\text{S}_4\text{N}_4 + 2\text{CS}_2 = \text{S} + (\text{CNS})_2 + \text{N}_2\text{S}_5$. Its alcoholic solution is violet. If the compounds spoken of in note 40 be added to the above nitrogen compounds of sulphur, it will be seen how varied may be the combinations of elements, like sulphur, able to form compounds of two types RX_5 —like nitrogen and RX_6 .

H_2 , forming H_2O , H_2S , H_2Se , and H_2Te .^{78b} The hydrogen compounds of selenium and tellurium are acids like hydrogen sulphide. Selenium, by simple heating in a stream of hydrogen, partially combines with it directly, but seleniuretted hydrogen is more readily decomposable by heat than sulphuretted hydrogen, and this property is still more developed in telluretted hydrogen. Hydrogen selenide and telluride are gases like sulphuretted hydrogen, and, like it, are soluble in water, form saline compounds with alkalis, precipitate metallic salts, are obtained by the action of acids on their compounds with metals, &c. Selenium and tellurium, like sulphur, give two normal grades of combination with oxygen, both of an acid character, of which only the forms corresponding to sulphurous anhydride—namely, selenious anhydride, SeO_2 , and tellurous anhydride, TeO_2 ⁷⁹—are formed directly.

^{78b} Telluretted hydrogen, TeH_2 , was obtained (Davy) by electrolysis, by the action of HCl on an alloy of tellurium and zinc, and by the action of water or dilute acids on Al_3Te_3 (Engel, Forcrand, and others). It is a very unstable colourless gas, which colours solutions of the alkalis red, and liquefies at about 0° into a liquid of sp. gr. 2.5 which freezes at about -50° . It forms unstable compounds with metals.

⁷⁹ **Selenious anhydride**, SeO_2 , is a volatile (at about 320°) solid, which crystallises in prisms soluble in water. It is best procured by the action of nitric acid on selenium. The well-known researches of Nilson (1874) showed that the salts of selenious acid readily form acid salts, and are so characteristic in many respects that they may even serve for judging the analogy of types of oxides. Thus, the oxides of the composition RO give normal salts of the composition $RSeO_3 \cdot 2H_2O$, where $R = Mn, Co, Ni, Cu, Zn$. The salts of magnesium, barium, and calcium contain a different quantity of water, as also do the salts of the oxides R_2O_3 . We may here turn attention to the fact that beryllium gives a normal salt, $BeSeO_3 \cdot 2H_2O$, and not a salt analogous to those of aluminium, scandium, $Sc_2(SeO_3)_3 \cdot H_2O$, yttrium, $Y_2(SeO_3)_3 \cdot 12H_2O$, and other oxides of the form R_2O_3 , which speaks in favour of the formula BeO .

Tellurous anhydride is also a colourless solid, which crystallises in octahedra: it also, when heated, first fuses and then volatilises. It is insoluble in water, and the decomposition of its salts gives a hydrate, H_2TeO_3 , which is insoluble.

It is a very characteristic circumstance that selenious and tellurous anhydrides are very easily **reduced** to selenium and tellurium. This is not only effected by metals like zinc, or by sulphuretted hydrogen, which are powerful deoxidisers, but even by sulphurous anhydride, which is able to precipitate selenium and tellurium from solutions of the selenites and tellurites, and even of the acids themselves, which is taken advantage of in obtaining these elements and separating them from sulphur.

Sulphuric acid, as we know, rarely acts as an oxidising agent. It is otherwise with selenic and telluric acids, H_2SeO_4 and H_2TeO_4 , which are powerful oxidising agents—that is, are easily reduced in many circumstances either into the lower oxide or even to selenium and tellurium. A powerful oxidising agent is required in order to convert selenious and tellurous anhydrides into selenic and telluric anhydrides, and, moreover, it must be employed in excess. If chlorine is passed through a solution of potassium selenide, K_2Se , telluride, K_2Te , selenite, K_2SeO_3 , or tellurite, K_2TeO_3 , it acts as an oxidiser in the presence of the water, forming potassium selenate, K_2SeO_4 , or tellurate, K_2TeO_4 . The same salts are formed by fusing the lower oxides with nitre. These salts are isomorphous with the corresponding sulphates, and cannot therefore be separated from them by crystallisation. The salts of potassium, sodium, magnesium, copper, cadmium, &c., are soluble like the sulphates, but those of barium and calcium are insoluble, in perfect analogy with the sulphates. When copper selenate, $CuSeO_4$, is treated with sulphuretted hydrogen (CuS

In distinction from sulphur these are both solids, obtained by the combustion of the elements themselves, like SO_2 , and by the action of oxidising agents on them. They form feebly energetic acids, having distinct dibasic properties; however a characteristic difference from SO_2 is observable, not so much in the physical properties of these compounds, as in their stability and capacity for further oxidation, just as in the series of the halogens already known to us, only in an inverse order; in the latter we saw that iodine combines more easily than bromine or chlorine with oxygen, forming more stable oxygen compounds, whereas, on the contrary, selenious and tellurous anhydrides are oxidised with difficulty and easily reduced, even by means of sulphurous acid.

Selenium was obtained in 1817 by Berzelius from the sublimate which collects in the first chamber in the preparation of sulphuric acid from Fahlun pyrites. Certain other pyrites also contain small

is precipitated), **selenic acid** remains in solution. On evaporation and drying *in vacuo* at 180° , it gives a syrupy liquid, which may be concentrated to almost the pure acid, H_2SeO_4 , having a specific gravity of 2.6. Cameron and Macallan (1891) showed that pure H_2SeO_4 only remains liquid in a state of superfusion, whilst the solidified acid melts at $+58^\circ$; the solid acid crystallises well, its sp. gr. being then 2.95. The hydrate $\text{H}_2\text{SeO}_4 \cdot \text{H}_2\text{O}$ melts at $+25^\circ$. The acid in a superfused state has a sp. gr. 2.36, that of the solid being 2.63. Like sulphuric acid, strong selenic acid attracts moisture from the atmosphere; it is not decomposed by sulphurous acid, but oxidises hydrochloric acid (like nitric, chromic, and manganic acids), evolving chlorine and forming selenious acid, $\text{H}_2\text{SeO}_4 + 2\text{HCl} = \text{H}_2\text{SeO}_3 + \text{H}_2\text{O} + \text{Cl}_2$. **Telluric acid**, H_2TeO_4 , is obtained by fusing tellurous anhydride with potassium hydroxide and chlorate; the solution, containing potassium tellurate, is then precipitated with barium chloride, and the barium tellurate, BaTeO_4 , obtained in the precipitate is decomposed by sulphuric acid. A solution of telluric acid is thus obtained, which on evaporation yields colourless prisms soluble in water, and of the composition $\text{TeH}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$. These two equivalents of water are driven off at 160° ; on further heating the last equivalent of water is expelled, and then oxygen is given off. It also gives chlorine with hydrochloric acid, like selenic acid. Its salts also correspond with those of sulphuric acid. It must, however, be remarked that telluric and selenic acids are able to give poly-acid salts with much greater ease than sulphuric acid. Thus, for example, there are known for telluric acid not only $\text{K}_2\text{TeO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{KHTeO}_4 \cdot 3\text{H}_2\text{O}$, but also $\text{KHTeO}_4 \cdot \text{H}_2\text{TeO}_4 \cdot \text{H}_2\text{O} = \text{K}_2\text{TeO}_4 \cdot 3\text{H}_2\text{TeO}_4 \cdot 2\text{H}_2\text{O}$. This salt is easily obtained from acid solutions of the preceding salts, and is less soluble in water. As selenious anhydride is volatile and gives similar poly-salts, it may be surmised that selenious, tellurous, selenic, and telluric anhydrides are polymeric as compared with sulphurous and sulphuric anhydrides, for which reason it would be desirable to determine the vapour density of selenious anhydride. It would probably correspond with Se_2O_4 or Se_3O_6 .

In order to show the very close analogy of selenium to sulphur, I shall quote two examples. Potassium cyanide dissolves selenium, as it does sulphur, forming potassium selenocyanate, KCNSe , corresponding with potassium thiocyanate. Acids precipitate selenium from this solution, because selenocyanic acid, HCNSe , when in a free state is immediately decomposed. A boiling solution of sodium sulphite dissolves selenium, just as it would sulphur, forming a salt analogous to thiosulphate of sodium, namely, sodium selenosulphate, Na_2SSeO_4 . Selenium is separated from a solution of this salt by the action of acid.

quantities of selenium. Some native selenides, especially those of lead, mercury, and copper, have been found in the Hartz Mountains, but only in small quantities. Pyrites and blendes, in which the sulphur is partially replaced by selenium, still remain the chief source for its extraction. When these pyrites are roasted they evolve selenious anhydride, which condenses in the cooler portions of the roasting apparatus, and is partially or wholly reduced by the sulphurous anhydride simultaneously formed. The presence of selenium in ores and sublimates is most simply tested by heating them before the blowpipe, when they evolve the characteristic odour of garlic. Selenium exhibits two modifications, like sulphur: one amorphous and insoluble in carbon bisulphide, the other crystalline and slightly soluble in carbon bisulphide (in 1,000 parts at 45° and 6,000 at 0°), and separating from its solutions in monoclinic prisms. If the red precipitate obtained by the action of sulphurous anhydride on selenious anhydride is dried, it gives a brown powder, having a specific gravity of 4.26, which when heated changes colour and fuses to a metallic mass, becoming lustrous as it cools. The selenium acquires different properties according to the rate at which it is cooled from a fused state; if rapidly cooled, it remains amorphous and has the same specific gravity (4.28) as the powder; but if slowly cooled it becomes crystalline and opaque, soluble in carbon bisulphide, and has a specific gravity of 4.80. In this form it fuses at 214° and remains unchanged, whilst the amorphous form, especially above 80° , gradually passes into the crystalline variety. The transition is accompanied by the evolution of heat, as in the case of sulphur; so that the analogy between sulphur and selenium is here clearly shown. In the fused amorphous form, selenium presents a brown mass, slightly translucent, with a vitreous fracture, whilst in the crystalline form it has the appearance of a grey metal, with a feeble lustre and a crystalline fracture.^{79a} Selenium boils at 700° , forming a vapour the density of which is only constant at a temperature of about 1400° , when it is equal to 79.4 (referred to hydrogen)—that is, the molecular formula is Se_2 , as with sulphur at an equally high temperature.

Tellurium is met with still more rarely than selenium (in Saxony)

^{79a} Muthmann, in his researches on the allotropic forms of selenium, pointed out (1889) a peculiar modification, which appears, as it were, as a transition between crystalline and amorphous selenium. It is obtained together with the crystalline variety by slowly evaporating a solution of selenium in bisulphide of carbon, and differs from the crystalline variety in the form of its crystals; it passes into the latter modification when heated. Schultz (1885) and subsequently Gutbier (1902) also obtained selenium (like Ag; see Chap. XXIV.) in a soluble form by the interaction of dilute solutions of SeO_2 and hydrate of hydrazine; but these researches are not so conclusive as those upon soluble silver, and we shall therefore not consider them more fully. Tellurium has also been obtained in a soluble colloidal state.

in combination with gold, silver, lead, and antimony in the so-called foliated tellurium ore. Bismuth telluride and silver telluride have been found in Hungary and in the Altai. Tellurium is extracted from bismuth telluride by mixing the finely powdered ore with potassium and charcoal in as intimate a mixture as possible, and then heating in a covered crucible. Potassium telluride, K_2Te , is then formed, because the charcoal reduces potassium tellurite. As potassium telluride is soluble in water, forming a red-brown solution, which is decomposed by the oxygen of the atmosphere ($K_2Te + O + H_2O = 2KHO + Te$), the mass formed in the crucible is treated with boiling water and filtered as rapidly as possible, and the resultant solution exposed to the air, by which means the tellurium is precipitated.⁸⁰ In a free state tellurium has a perfectly **metallic appearance**; it is of a silver-white colour, crystallises very easily in long brilliant needles, is very brittle, so that it can be easily reduced to powder, but is a bad conductor of heat and electricity, and in this respect, as in many others, it forms a transition from the metals to the non-metals. Its specific gravity is 6.18, it melts at an incipient red heat, and takes fire when heated in air, like selenium and sulphur, burning with a blue flame, evolving white fumes of tellurous anhydride, TeO_2 , and emitting an acrid smell if no selenium is present; but if it contains selenium, the odour of the latter preponderates. Alkalies dissolve tellurium when boiled with it, potassium telluride, K_2Te , and potassium tellurite, K_2TeO_3 , being formed. The solution is of a red colour, owing to the presence of the telluride, K_2Te ; but the

⁸⁰ The tellurium thus prepared is impure, and contains a large amount of selenium. The latter may be removed by converting the mixture into the salts of potassium and treating these with nitric acid and barium nitrate, when barium selenate only is precipitated, whilst the barium tellurate remains in solution. This method does not, however, give a pure product, and it appears to be best to separate the selenium from the tellurium in a metallic form; this is done by boiling the impure potassium tellurate with hydrochloric acid, which converts it into potassium tellurite, from which the tellurium is reduced by sulphurous anhydride. The metal thus obtained is then fused and distilled in a stream of hydrogen; the selenium volatilises first, and then the tellurium, which is much less volatile than the former. Nevertheless, tellurium is also volatile, and may be separated in this manner from less volatile metals, such as antimony. Brauner showed (1889) that tellurium purified by the usual method, even after distillation, contains a large amount of impurities. The atomic weight of Te has been the object of repeated investigation; and although in recent years (1889-1902) many (Brauner, Mether, Chikashigé, Köthner, Pellini, Guthrie, and others) have found it to lie between 127.3 and 127.9 ($O = 16$), the mean being 127.7, i.e., greater than that of iodine (about 126.9), yet Steiner (1901) by analysing the volatile $(C_6H_5)_2Te$, found $Te = 126.4$, which is less than for iodine. My personal opinion is that the atomic weights of iodine (see Chap. XI., note 62) and tellurium are very near 127 ($O = 16$), and that only experiment and very careful fresh researches can prove which is the greater, although it seems to me more probable that I is slightly greater than Te, as it should be according to the periodic law, and that the iodine experimented on contained traces of Cl and Br, and that its atomic weight is greater than 127. This question must be decided by future investigators.

colour disappears when the solution is cooled or diluted, the tellurium being all precipitated : $2K_2Te + K_2TeO_3 + 3H_2O = 6KHO + 3Te$.⁸¹

⁸¹ The decomposition proceeds in the above order in the cold, but in a hot solution with an excess of potassium hydroxide it proceeds inversely. A similar phenomenon takes place when tellurium is fused with alkalies, and it is therefore necessary in order to obtain potassium telluride to add charcoal.

Selenium and tellurium form higher compounds with chlorine with comparative ease. For selenium, $SeCl_2$ and $SeCl_4$ are known, and for tellurium $TeCl_2$ and $TeCl_4$. The tetrachlorides of selenium and tellurium are formed by passing chlorine over these elements. Selenium tetrachloride, $SeCl_4$, is a crystalline volatile mass which gives selenious anhydride and hydrochloric acid with water. Tellurium tetrachloride is much less volatile, fuses easily, and is also decomposed by water. Both elements form similar compounds with bromine. Tellurium tetrabromide is red, fuses to a brown liquid, volatilises, and gives a crystalline salt, $K_2TeBr_6 \cdot 3H_2O$, with an aqueous solution of potassium bromide.

CHAPTER XXI

CHROMIUM, MOLYBDENUM, TUNGSTEN, URANIUM, AND MANGANESE

SULPHUR, selenium, and tellurium belong to the uneven series of the sixth group. In the even series of this group there are known **chromium, molybdenum, tungsten, and uranium**; these give oxides of the type RO_3 , like SO_3 . Their acid properties are less sharply defined than those of sulphur, selenium, and tellurium, as is the case with all elements of the even series as compared with those of the uneven series in the same group. But still the oxides CrO_3 , MoO_3 , WO_3 , and even UO_3 , form salts of the composition MO, nRO_3 with bases MO . In the case of the heavy elements, and especially of uranium, the type of oxide, UO_3 , is less acid and more basic, because in the even series of oxides the element with the highest atomic weight always acquires a more and more pronounced basic character. Hence UO_3 shows the properties of a base, and gives salts, UO_2X_2 . The basic properties of chromium, molybdenum, tungsten, and uranium are most clearly expressed in the lower oxides, which they all form. Thus chromic oxide, Cr_2O_3 , is as distinct a base as alumina, Al_2O_3 .

Of all these elements **chromium** is the most widely distributed in nature and the most frequently used. It gives chromic anhydride, CrO_3 , and chromic oxide, Cr_2O_3 —two compounds whose relative amounts of oxygen stand in the ratio 2 : 1. Chromium is, although somewhat rarely, met with in nature as a compound of one or the other type. The red chromium ore of the Urals, lead chromate or crocoisite, $PbCrO_4$, was the source in which chromium was discovered by Vauquelin, who gave it this name (from the Greek word *χρῶμα*, signifying colour) owing to the brilliant colours of its compounds; the chromates (salts of chromic anhydride) are red and yellow, and the chromic salts (from Cr_2O_3), green and violet. The red lead chromate is, however, very rare. Chromic oxide, Cr_2O_3 , is more frequently met with. In small quantities it forms the colouring matter of many minerals and rocks—for example, of some serpentines. The commonest ore, and the chief source of the chromium compounds, is **chrome iron ore**, or chromite, which occurs in the

Urals¹ and Asia Minor, California, Australia, and other localities. This is magnetic iron ore, $\text{FeO}, \text{Fe}_2\text{O}_3$, in which the ferric oxide is replaced by chromic oxide, its composition being $\text{FeO}, \text{Cr}_2\text{O}_3$. Chrome iron ore crystallises in octahedra of sp. gr. 4.4; it has a feeble metallic lustre, is of a greyish-black colour, and gives a brown powder. It is very feebly acted on by acids, but when fused with acid potassium sulphate it gives a soluble mass, which contains a chromic salt, besides potassium and ferrous sulphates. In practice the treatment of chrome iron ore is mainly carried on for the preparation of chromates, and not of chromic salts, and therefore we shall trace the history of the element by beginning with chromic acid, and especially with the working up of the chrome iron ore into **potassium dichromate**, $\text{K}_2\text{Cr}_2\text{O}_7$, as the most common salt of this acid. It must be remarked that chromic anhydride, CrO_3 , is only obtained in an anhydrous state, and is distinguished for its capacity for easily giving anhydro-salts with the alkalies, containing one, two, and even three equivalents of the anhydride to one equivalent of base. Thus, among the potassium salts there is known the normal or yellow chromate, K_2CrO_4 , which corresponds to, and is perfectly isomorphous with, potassium sulphate. As in the presence of a certain excess of acid, the dichromate ($\text{K}_2\text{Cr}_2\text{O}_7 = 2\text{K}_2\text{CrO}_4 + 2\text{HX} - 2\text{KX} - \text{H}_2\text{O}$) is easily formed from K_2CrO_4 , the object of the manufacturer is to produce such a dichromate, the more so as it contains a larger proportion of the elements of chromic acid than the normal salt. Finely ground chrome iron ore, when heated with an alkali, absorbs oxygen almost as easily (Chap. III., note 7) as a mixture of the oxides of manganese with an alkali. The chromic oxide is oxidised into the anhydride, $\text{Cr}_2\text{O}_3 + \text{O}_3 = 2\text{CrO}_3$, and then combines with the alkali. As the oxidation and formation of the chromate proceed, the mass turns *yellow*. The iron is also oxidised, forming Fe_2O_3 .

A mixture of lime (sometimes with potash) and chrome iron ore is heated in a reverberatory furnace, with free access of air and at a red heat for several hours, until the mass becomes yellow; it then contains normal calcium chromate, CaCrO_4 , which is insoluble in water in the presence of an excess of lime.^{1a} The resultant mass is ground up, and treated with water and sulphuric acid. The excess of lime forms gypsum, and the soluble calcium dichromate, CaCr_2O_7 , together with a certain amount of iron, passes into solution. The solution is poured off

¹ The working of the Ural chrome iron ore into chromium compounds has been firmly established in Russia, thanks to the endeavours of P. K. Ushkoff, who constructed large works for this purpose on the river Kama, near Elabougi.

^{1a} But the calcium chromate is soluble in water in the presence of an excess of chromic acid, as may be seen from the fact that a solution of chromic acid dissolves lime.

and chalk added to it; this precipitates the ferric oxide and forms a fresh quantity of gypsum, while the chromic acid remains in solution—that is, it does not form the sparingly soluble normal salt (1 part soluble in 240 parts of water). The solution then contains a fairly pure calcium dichromate, which by double decomposition gives other chromates; for example, with a solution of potassium sulphate it gives a precipitate of calcium sulphate and a solution of potassium dichromate, which crystallises when evaporated.²

Potassium dichromate, $K_2Cr_2O_7$, readily crystallises from acid solutions in red, well-formed prismatic crystals, which fuse at a red heat and evolve oxygen at a very high temperature, leaving chromic oxide and the normal salt, which undergoes no further change: $2K_2Cr_2O_7 = 2K_2CrO_4 + Cr_2O_3 + O_3$. At the ordinary temperature 100 parts of water dissolve 10 parts of this salt, and the solubility increases as the temperature rises. It is most important to note that the dichromate does not contain water; it is $K_2CrO_4 + CrO_3$; the acid salt corresponding to acid potassium sulphate, $KHSO_4$, does not exist. In dissolving in water, it produces cold, i.e., it does not form a very stable compound with water. The solution and the salt itself are poisonous, and act as powerful oxidising agents, which is the character of chromic acid in general. When heated with sulphur or organic substances, with sulphurous anhydride, hydrogen sulphide, &c., this salt is deoxidised, yielding chromic compounds.^{2a} Potassium dichromate³ is used in the

² There are many variations in the details of the manufacturing processes, and these must be looked for in works on technical chemistry. But we may add that the chromate may also be obtained by slightly roasting briquettes of a mixture of chrome iron and lime and then leaving the resultant mass to the action of moist air (oxygen is absorbed, and the mass turns yellow). The sodium salt, $Na_2Cr_2O_7 \cdot 2H_2O$, is now most frequently used in practice. It dissolves readily in water.

^{2a} The oxidising action of potassium dichromate on organic substances at the ordinary temperature is especially marked under the action of light. Thus it acts on gelatin, as Poutven discovered; this is applied to photography in the processes of photogravure, photo-lithography, pigment printing, &c. Under the action of light this gelatin is oxidised (and the chromic anhydride deoxidised), forming a compound insoluble in warm water, whilst where the light has not acted, the gelatin remains soluble, its properties being unaffected by the presence of chromic acid or potassium dichromate. A mixture of $Na_2Cr_2O_7$ with a small quantity of glycerine takes fire when heated to 100° , leaving a pulverulent mass of oxide of chromium; the glycerine is oxidised.

³ Ammonium and sodium dichromates are now also prepared on a large scale. The sodium salts may be prepared in exactly the same manner as those of potassium. The normal salt crystallises with ten equivalents of water, like Glauber's salt, with which it is isomorphous. Its solution above 30° deposits the anhydrous salt. Sodium dichromate crystals have the composition $Na_2Cr_2O_7 \cdot 2H_2O$. The ammonium salts of chromic acid are obtained by saturating the anhydride itself with ammonia. The dichromate is obtained by saturating one part of the anhydride with ammonia and then adding a second part of anhydride and evaporating under the receiver of an air-pump. On ignition, the ammonium salts leave chromic oxide. Potassium ammonium chromate, NH_4KCrO_4 , is

arts and in chemistry as a source for the preparation of all other chromium compounds. It is converted into yellow pigments by means of double decomposition with salts of lead, barium, and zinc. When solutions of the salts of these metals are mixed with potassium dichromate (in dyeing generally mixed with soda, in order to obtain normal salts), they are precipitated as insoluble normal salts; for example, $2\text{BaCl}_2 + \text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{O} = 2\text{BaCrO}_4 + 2\text{KCl} + 2\text{HCl}$. It follows from this that these salts are insoluble in dilute acids, but the precipitation is not complete (as it would be with the normal salt). The barium and zinc salts are of a lemon-yellow colour; the lead salt has a still more intense colour, passing into orange. Yellow cotton prints are dyed with this pigment. The silver salt, Ag_2CrO_4 , is of a bright-red colour.

When potassium dichromate is mixed with potassium hydroxide or carbonate (carbonic anhydride being disengaged in the latter case) it forms the normal salt, K_2CrO_4 , known as **yellow chromate of potassium**. Its specific gravity is 2.7, being almost the same as that of the dichromate. It absorbs heat in dissolving; one part of the salt dissolves in 1.75 part of water at the ordinary temperature, forming a yellow solution. When mixed with even such feeble acids as acetic, and more especially with the ordinary acids, it gives the dichromate, and Graham obtained a trichromate, $\text{K}_2\text{Cr}_3\text{O}_{10} = \text{K}_2\text{CrO}_4 \cdot 2\text{CrO}_3$, by mixing a solution of the dichromate with an excess of nitric acid.

obtained in yellow needles from a solution of potassium dichromate in aqueous ammonia; it loses ammonia and becomes converted into potassium dichromate not only when ignited, but also by degrees at the ordinary temperature. This shows the feeble energy of chromic acid, and its tendency to form stable dichromates. Magnesium chromate is soluble in water, as also is the strontium salt. The calcium salt is also somewhat soluble, but the barium salt is almost insoluble. The isomorphism with sulphuric acid is shown in the chromates by the fact that the magnesium and ammonium salts form double salts containing six equivalents of water, which are perfectly isomorphous with the corresponding sulphates. The magnesium salt crystallises in large crystals containing seven equivalents of water. The beryllium, cerium, and cobalt salts are insoluble in water. Chromic acid dissolves manganous carbonate, but on evaporation the solution deposits manganese dioxide, formed at the expense of the oxygen of the chromic acid. Chromic acid also oxidises ferrous oxide, and the hydroxide is soluble in chromic acid.

One of the chromates most used by the dyer is the insoluble yellow lead chromate, PbCrO_4 (Chap. XVIII., note 46), which is precipitated on mixing solutions of PbX_2 with soluble chromates. It easily forms a basic salt, having the composition $\text{PbO} \cdot \text{PbCrO}_4$, as a crystalline powder, obtained by fusing the normal salt with nitre and then rapidly washing in water. The same substance is obtained, although impure and in small quantity, by treating lead chromate with neutral potassium chromate, especially on boiling the mixture; and this gives the possibility of attaining, by means of those materials, various tints of lead chromate, from yellow to red, passing through different shades of orange. The decomposition which takes place (incompletely) in this case is as follows: $2\text{PbCrO}_4 + \text{K}_2\text{CrO}_4 = \text{PbCrO}_4 \cdot \text{PbO} + \text{K}_2\text{Cr}_2\text{O}_7$ —that is, potassium dichromate is formed in solution. A hot solution of AgNO_3 and K_2CrO_4 in the presence of nitric acid gives dichromate of silver, $\text{Ag}_2\text{Cr}_2\text{O}_7$, in the form of a crystalline precipitate, which is decomposed by water into $\text{Ag}_2\text{CrO}_4 + \text{CrO}_3$ (Autenrieth).

Chromic anhydride is obtained by preparing a saturated solution of potassium dichromate at the ordinary temperature and pouring it in a thin stream into an equal volume of pure sulphuric acid.⁴ On mixing, the temperature naturally rises; when slowly cooled, the solution deposits chromic anhydride in red needle-shaped crystals, sometimes several centimetres long. The crystals are freed from the mother liquor by placing them on a porous tile.^{4a} It is very important at this point to call attention to the fact that a hydrate of chromic anhydride is never obtained in the decomposition of chromic compounds, but always the anhydride, CrO_3 . The corresponding hydrate, CrO_4H_2 , or any other hydrate, is not even known. Nevertheless, it must be admitted that chromic acid is dibasic, because it forms salts isomorphous or perfectly analogous with the salts formed by sulphuric acid, which is the best example of a dibasic acid. A proof of this is seen in the fact that the anhydride and salts give (when heated with sodium chloride and sulphuric acid) a volatile chloranhydride, CrO_2Cl_2 , containing two atoms of chlorine, as a dibasic acid should.⁵ Chromic anhydride is a red

⁴ The sulphuric acid should not contain any lower oxides of nitrogen, because these reduce chromic anhydride to chromic oxide. If a solution of a chromate is heated with an excess of acid—for instance, sulphuric or hydrochloric acid—oxygen or chlorine is evolved, and a solution of a chromic salt is formed. One of the first methods by which CrO_3 was obtained consisted in converting its salts into volatile **chromium hexafluoride**, CrF_6 . This compound was obtained by Unverdorphen by mixing lead chromate with fluor spar in a dry state and treating the mixture with fuming sulphuric acid in a platinum vessel: $\text{PbCrO}_4 + 3\text{CaF}_2 + 4\text{H}_2\text{SO}_4 = \text{PbSO}_4 + 3\text{CaSO}_4 + 4\text{H}_2\text{O} + \text{CrF}_6$. Chromium fluoride is volatile, and forms a very caustic, poisonous vapour, which condenses when cooled in a dry platinum vessel into a red exceedingly volatile liquid, fuming strongly in the air. The vapours of this substance when introduced into water are decomposed into hydrofluoric acid and chromic anhydride: $\text{CrF}_6 + 3\text{H}_2\text{O} = \text{CrO}_3 + 6\text{HF}$. If very little water is taken the hydrofluoric acid volatilises, and chromic anhydride separates directly in crystals. The chloranhydride of chromic acid, CrO_2Cl_2 (note 5), is also decomposed in the same manner. A solution of chromic acid and a precipitate of barium sulphate are formed by treating the insoluble barium chromate with an equivalent quantity of sulphuric acid. If carefully evaporated, the solution yields crystals of chromic anhydride. Fritzsche gave a very convenient method of preparing chromic anhydride, based on the relation of chromic to sulphuric acid. At the ordinary temperature the strong acid dissolves both chromic anhydride and potassium chromate, but if a certain amount of water is added to the solution the chromic anhydride separates, and if the amount of water is increased the precipitated chromic anhydride is again dissolved. The chromic anhydride is almost all separated from the solution when it contains two equivalents of water to one of sulphuric acid.

^{4a} They cannot be filtered through paper or washed, because the chromic anhydride is reduced by the filter paper, and is dissolved during the process of washing.

⁵ Berzelius observed, and Rose carefully investigated, this remarkable reaction, which occurs between chromic acid and sodium chloride in the presence of sulphuric acid. If 10 parts of common salt are mixed with 12 parts of potassium dichromate, fused, cooled, broken up into lumps, and covered with 20 parts of fuming sulphuric acid, it gives rise to a violent reaction, accompanied by the formation of brown fumes of **chromic chloranhydride**, or **chromyl chloride**, CrO_2Cl_2 , according to the reaction: $\text{CrO}_3 + 2\text{NaCl} + \text{H}_2\text{SO}_4 = \text{Na}_2\text{SO}_4 + \text{H}_2\text{O} + \text{CrO}_2\text{Cl}_2$. The addition of an excess of sulphuric acid is

crystalline substance, which is converted into a black mass by heat; it fuses at 190° , and disengages oxygen above 250° , leaving a residue of chromium dioxide, CrO_2 ,⁶ and, on still further heating, chromic oxide, Cr_2O_3 . Chromic anhydride is exceedingly soluble in water, and even attracts moisture from the air; but, as was mentioned above, it does not form any definite compound with water. The specific gravity of its crystals is 2.7, and when fused it has a specific gravity 2.6. The solution presents perfectly defined acid properties. It liberates carbonic anhydride from carbonates; gives insoluble precipitates of the chromates with salts of barium, lead, silver, and mercury.

necessary in order to retain the water. The same substance is always formed when a metallic chloride is heated with chromic and sulphuric acids. With CrO_3 , a strong solution of HCl or gaseous HCl directly forms water and CrO_2Cl_2 , but this compound is decomposed by an excess of water. The formation of this volatile substance is easily observed, owing to the brown colour peculiar to its vapour. On condensing the vapour in a dry receiver, a liquid is obtained having a sp. gr. of 1.9, boiling at 118° , and having the vapour density 78, which corresponds with the above formula. Chromyl chloride is decomposed by heat into chromic oxide, oxygen, and chlorine: $2\text{CrO}_2\text{Cl}_2 = \text{Cr}_2\text{O}_3 + 2\text{Cl}_2 + \text{O}$; so that it is able to act simultaneously as a powerful oxidising and chlorinating agent. When brought into contact with inflammable substances it often sets fire to them; for instance, phosphorus, sulphur, oil of turpentine, ammonia, hydrogen, and other substances. It attracts moisture from the atmosphere with great energy, and must therefore be kept in closed vessels. It dissolves iodine and chlorine, and even forms a solid compound with the latter, which depends upon the faculty of chromium to form its higher oxide, Cr_2O_7 . The close analogy in physical properties of the chloranhydrides, CrO_2Cl_2 and SO_2Cl_2 , is very remarkable, although sulphurous anhydride is a gas, and the oxide, CrO_2 (which is mentioned in the following note), a non-volatile solid.

If three parts of potassium dichromate are mixed with four parts of strong hydrochloric acid and a small quantity of water, and gently warmed, it all passes into solution, and no chlorine is evolved; on cooling, the liquid deposits red prismatic crystals, known as **Peligt's salt**, very stable in air. This has the composition KCl, CrO_3 , and is formed according to the equation, $\text{K}_2\text{Cr}_2\text{O}_7 + 2\text{HCl} = 2\text{KCl}, \text{CrO}_3 + \text{H}_2\text{O}$. It is evident that this is the first chloranhydride of chromic acid, HCrO_3Cl , in which the hydrogen is replaced by potassium. It is decomposed by water, and on evaporation the solution yields potassium dichromate and hydrochloric acid. This is a fresh instance of the reversible reactions so frequently encountered. With sulphuric acid Peligt's salt forms chromyl chloride. Geuther produced Peligt's salt from potassium chromate and chromyl chloride. When heated, it parts with all its chlorine, and on further heating gives chromic oxide.

⁶ This dioxide, CrO_2 , may also be obtained by mixing solutions of chromic salts with solutions of chromates. The brown precipitate formed contains a compound, $\text{Cr}_2\text{O}_3, \text{CrO}_3$, consisting of equivalent amounts of chromic oxide and anhydride. The brown precipitate of chromium dioxide contains water. The same substance is formed by the imperfect deoxidation of chromic anhydride by various reducing agents. Chromic oxide, when heated, absorbs oxygen, and appears to give the same substance. Chromic nitrate, when ignited, gives CrO_2 . When CrO_2 is ignited it disengages oxygen, chromic oxide being left. It is the analogue of manganese dioxide. Krüger treated chromium dioxide with a mixture of sodium chloride and sulphuric acid, and found that chlorine gas was evolved, but that chromyl chloride was not formed. Under the action of light, a solution of chromic acid also deposits the brown dioxide. At the ordinary temperature chromic anhydride leaves a brown stain upon the skin and tissues, which probably proceeds from a decomposition of the same kind. Chromic anhydride is soluble in alcohol containing water, and this solution is decomposed in a similar manner by light. Chromium dioxide forms K_2CrO_4 when treated with H_2O_2 in the presence of KHO .

The action of hydrogen peroxide on a solution of chromic acid or of potassium dichromate gives a blue solution, which very quickly becomes colourless with the disengagement of oxygen. Barreswill showed that this is due to the formation of a **perchromic anhydride**, Cr_2O_7 . This peroxide is remarkable from the fact that it very easily dissolves in ether and is much more stable in this solution, so that, by shaking up hydrogen peroxide mixed with a small quantity of chromic acid with ether, it is possible to transfer all the blue substance formed to the ether.^{6a}

When heated with oxygen acids, chromic acid evolves oxygen; for example, with sulphuric acid the following reaction takes place: $2\text{CrO}_3 + 3\text{H}_2\text{SO}_4 = \text{Cr}_2(\text{SO}_4)_3 + \text{O}_3 + 3\text{H}_2\text{O}$. It will be readily understood from this that a **mixture of chromic acid or of its salts with sulphuric acid** forms an excellent **oxidising agent**, which is frequently employed in chemical laboratories and for technical purposes as a means of oxidation. Thus hydrogen sulphide and sulphurous anhydride are converted into sulphuric acid by this means. Chromic acid is able to act as a powerful oxidising agent because it passes into chromic oxide, and in so doing disengages half of the oxygen contained in it: $2\text{CrO}_3 = \text{Cr}_2\text{O}_3 + \text{O}_3$.^{6b} In acting on a solution of potassium iodide, CrO_3 , like many other oxidising agents, liberates iodine; the reaction proceeds in proportion to the amount of CrO_3 present, and may serve for determining the amount of CrO_3 , since the quantity of iodine liberated can be accurately determined by the iodometric method (Chap. XX., note 42). If chromic anhydride be ignited in a stream of ammonia, it gives chromic oxide, water, and nitrogen. In all cases when chromic acid acts as an oxidising agent in the presence of acids and under the action of heat, the product of its deoxidation is a chromic salt, CrX_3 , which is green, so that the **red or yellow solution** of a salt of chromic acid is then transformed into a **green** solution of a chromic salt, derived from chromic oxide, Cr_2O_3 , which is analogous to Al_2O_3 , Fe_2O_3 , and

^{6a} It might be supposed that perchromic anhydride, Cr_2O_7 , would correspond to perchromic acid, $\text{H}_2\text{Cr}_2\text{O}_8$, but as yet it is not certain whether corresponding salts are formed. Péchard (1891), on adding an excess of H_2O_2 and baryta water to a dilute solution of CrO_3 (8 grms. per litre), observed the formation of a yellow precipitate; but oxygen was disengaged at the same time, and the precipitate (which easily exploded when dried) was found to contain, besides an admixture of BaO_2 , a compound, BaCrO_5 , and this ($\text{BaO}_2 + \text{CrO}_3$) does not correspond with perchromic acid.

^{6b} Thus, chromic anhydride itself is a powerful oxidising agent, and is therefore employed instead of nitric acid in galvanic batteries (as a depolariser), the hydrogen evolved at the carbon being then oxidised, and the chromic acid converted into a non-volatile product of deoxidation, instead of yielding, as nitric acid does, volatile lower oxides of offensive odour. Organic substances are more or less perfectly oxidised by means of chromic anhydride, although this generally requires the aid of heat, and does not proceed in the presence of alkalis, but generally *in the presence of acids*.

other bases of the composition R_2O_3 . This analogy is seen in the insolubility of the anhydrous oxide, in the gelatinous form of the colloidal hydrate, in the formation of alums ⁷ and of a volatile anhydrous

⁷ As a mixture of potassium dichromate and sulphuric acid is usually employed for oxidation, the resultant solution generally contains a double sulphate of potassium and oxide of chromium—that is, **chrome alum**, $KCr(SO_4)_2 \cdot 12H_2O$. It is prepared by dissolving potassium dichromate in dilute sulphuric acid; alcohol is then added and the solution slightly heated (aldehyde, C_2H_5O , is disengaged) or sulphurous anhydride is passed through it. If the temperature of decomposition does not exceed 35° , a **violet** solution of chrome alum is obtained, but if the solution is heated, a solution of the same alum is obtained of a **green** colour. As chrome alum requires for solution 7 parts of water at the ordinary temperature, it follows that if a somewhat strong solution be taken, chrome alum will separate out on cooling. **If the liquid be heated somewhat strongly, for instance, to the boiling-point of water, it acquires a bright green colour, and on evaporation does not give any crystals whatever. If the green solution be kept, however, for several weeks at the ordinary temperature, it will deposit violet crystals of chrome alum.** The green solution, when evaporated, gives a non-crystalline mass. The transition of the green modification into the violet is accompanied by a decrease in volume (Lecoq de Boisbandran, Favre).

Not chrome alum alone, but all the chromic salts, give **green** and **violet modifications**. The green chromic salts, obtained by heating solutions of the violet salts, give violet solutions if kept for a long time. Chromic oxide, like alumina, is able to give both acid and basic salts. It is supposed that the difference between the green and violet salts is due to this fact. This opinion of Krüger is based on the fact that alcohol throws out from the green solution a salt which contains less sulphuric acid than the normal violet salt. On the other hand, Löwel showed that all the acid cannot be separated from the green chromic salts by suitable reagents, as easily as it can be from the same solution of the violet salts; thus barium salts do not precipitate all the sulphuric acid from solutions of the green salts. Recoura (1890–1896) showed that there are two kinds of green salts. If a solution of the crystalline violet chromium sulphate, $Cr_2(SO_4)_3 \cdot 8H_2O$, is boiled, it gives one variety, while if the crystals of the sulphate are cautiously heated they lose $10H_2O$, and give another variety, which forms the same green solution as the first. Recoura found that one equivalent of sulphuric acid is lost per 2 molecules of salt in the formation of the first variety, and that only one equivalent of sulphuric acid out of the five it contains reacts with $BaCl_2$, precipitating $BaSO_4$. He considers this first variety to contain a peculiar complex salt, $(Cr_4S_4O_{17})SO_4$, corresponding to a hydrate, and in general to $(Cr_4S_4O_{17})X_2$, or with the addition of water to $[Cr_4(SO_4)_4(OH)_2]X_2$. Hence from its composition, $4CrX_3$, this is a basic chromic salt. The other variety, having the composition of the normal neutral salt, $Cr_2(SO_4)_3$, gives no precipitate at all with a solution of BaX_2 , and is able to combine with yet another molecule of sulphuric acid or its salts, and the resulting salts are not precipitated by $BaCl_2$, but, after the addition of sulphuric acid, with CuX_2 give a precipitate of a copper salt of chromo-sulphuric acid, $(Cr_2S_4O_{16})Cu$. Recoura obtained compounds with 2, 3, 4, and $5H_2SO_4$, but they all give the above precipitate with cupric salts, and evolve more heat with bases than the sulphuric acid they contain. Wyrouboff (1902) applied to the abnormal (not directly reacting with $BaCl_2$) sulphate compounds of chromic oxide the view that their 'complex' properties are due to the fact that some of the hydroxyls in $Cr_2(OH)_6$ acquire the property of alcoholic hydroxyls; however, as no difference is to be seen between the hydroxyl in $Na(OH)$ and that in any alcohol, for instance, $CH_3(OH)$, the difference in the mode of reaction of NaX and CH_3X can only be ascribed to the difference between Na and CH_3 , or in the manner in which they are united with (OH) , and the cause of the peculiar reactions and of the isomerism of the violet and green compounds of chromic oxide cannot yet be considered as satisfactorily explained. And as similar 'complex' organic compounds (alcohols and others) are always composed of many elements, a portion of which are non-atomic, it appears to me that the explanation of this case

chloride of chromium, Cr_2Cl_6 , and in the employment of the hydrate as a mordant in dyeing, &c.⁸

should be sought in the same light as for the organic compounds (Vol. I., pp. 391 *et seq.*). For my part I think that here, as with the organic compounds, we require a number of well-investigated experimental data before looking for any explanation, and that as the chromic salts cannot be said to be thoroughly investigated (for instance, their molecular weights are unknown, and also their behaviour with respect to ammonia, the chloranhydrides and fluorides, &c.), this class of compounds ought to be regarded as a matter deserving detailed research.

Potassium and sodium hydroxides give a precipitate of the hydroxide with chromic salts, CrX_3 . The violet and green salts give a hydroxide soluble in an excess of the reagent; but the hydroxide is held in solution by very feeble affinities, so that it is partially separated by heat and dilution with water, and completely so on boiling. In an alkaline solution, chromic hydroxide is easily converted into chromic acid by the action of lead dioxide, chlorine, and other oxidising agents. If the chromic oxide occurs together with such oxides as magnesia, or zinc oxide, then on precipitation it separates out from its solution in combination with these oxides, forming, for example, $\text{ZnO}, \text{Cr}_2\text{O}_3$ (Viard). When fused with borax, chromic salts give a green glass. The same coloration is communicated to ordinary glass by the presence of traces of chromic oxide. A chrome glass containing a large amount of chromic oxide may be ground up and used as a green pigment. Among the hydrates of oxide of chromium **Guignet's green** forms one of the green pigments which have been substituted for the poisonous arsenical copper pigments (Schweinfurt's green). Guignet's green has an extremely bright-green colour, and is distinguished for its great stability, not only under the action of light but also towards reagents; thus, it is not altered by alkaline solutions, and even nitric acid does not act on it. This pigment remains unchanged up to a temperature of 250° ; it contains $\text{Cr}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$, and generally a small amount of alkali. It is prepared by fusing 3 parts of boric acid with 1 part of potassium dichromate; oxygen is disengaged, and a green glass, containing a mixture of the borates of chromium and potassium, is obtained. When cool this glass is ground up and treated with water, which extracts the boric acid and alkali and leaves the above-named chromic hydroxide behind. This hydroxide only parts with its water at a red heat, leaving the anhydrous oxide.

The chromic hydroxides lose their water by ignition, and in so doing become spontaneously incandescent, like the ordinary ferric hydroxide (Chap. XXII.). It is not known, however, whether all the modifications of chromic oxide show this phenomenon. The anhydrous **chromic oxide**, Cr_2O_3 , is exceedingly difficultly soluble in acids, if it has passed through the above recalcination. But if it has parted with its water, or the greater part of it, and not yet undergone this self-induced incandescence (has not lost a portion of its energy), it is soluble in acids. It is not reduced by hydrogen. The chromates of mercury and ammonium give a very convenient method for its preparation, because when ignited they leave chromic oxide behind. In the first instance, $2\text{Hg}_2\text{CrO}_4 = \text{Cr}_2\text{O}_3 + \text{O}_2 + 4\text{Hg}$, and in the second $(\text{NH}_4)_2\text{Cr}_2\text{O}_7 = \text{Cr}_2\text{O}_3 + 4\text{H}_2\text{O} + \text{N}_2$. The second reaction is very energetic, and the mass of salt burns spontaneously if the temperature is sufficiently high. A mixture of potassium sulphate and chromic oxide is formed by heating potassium dichromate with an equal weight of sulphur: $\text{K}_2\text{Cr}_2\text{O}_7 + \text{S} = \text{K}_2\text{SO}_4 + \text{Cr}_2\text{O}_3$. The sulphate is easily extracted by water, and there remains a bright-green residue of the oxide, the colour of which is more brilliant the lower the temperature of the decomposition. The oxide thus obtained is used as a green pigment for china and enamel. The crystalline anhydrous chromic oxide has a specific gravity of 5.2–5.6, and is almost black and gives a green powder. The crystals are hard enough to scratch glass, and have a metallic lustre. The crystalline form of chromic oxide is identical with that of the oxide of iron and alumina, with which it is isomorphous.

* The most important of the compounds corresponding with chromic oxide is **chromic chloride**, Cr_2Cl_6 , which is known in an anhydrous and a hydrated form. The former is insoluble in water, the latter easily dissolves, and on evaporation its solution leaves a

Chromic oxide, Cr_2O_3 , found rarely, and in small quantities, in chrome ochre, is formed by the oxidation of chromium and its lower

hygroscopic mass, which is very unstable and readily evolves hydrochloric acid when heated with water. The anhydrous form is of a violet colour, and according to Wöhler is formed by heating an intimate mixture of the anhydrous chromic oxide with carbon and organic matter in a stream of dry chlorine; a slightly volatile sublimate of chromic chloride, CrCl_3 , is thus formed. This substance forms **violet tabular crystals**, greasy to the touch and insoluble in water; but if they are powdered and boiled in water for a long time they pass into a **green solution**. Strong sulphuric acid does not act on the anhydrous salt, or only acts with exceeding slowness, like water. Even aqua regia and other acids do not act on the crystals, and alkalies only show a very feeble action. The specific gravity of the crystals is 2.99. When fused with sodium carbonate and nitre they give sodium chloride and potassium chromate, and when ignited in air they form green chromic oxide and evolve chlorine. On ignition in a stream of ammonia, chromic chloride forms sal-ammoniac and chromium nitride, CrN (analogous to the nitrides BN , AlN). Mosberg and Peligot showed that when chromic chloride is ignited in hydrogen, it parts with one-third of its chlorine, forming chromous chloride, CrCl_2 —that is, there is formed from a compound corresponding with chromic oxide, Cr_2O_3 , a compound answering to the **suboxide**, chromous oxide, CrO —just as hydrogen converts ferric chloride into ferrous chloride with the aid of heat. **Chromous chloride**, CrCl_2 , forms colourless crystals readily soluble in water, which, in dissolving, evolve a considerable amount of heat and form a blue liquid, capable of absorbing oxygen from the air with great facility, being converted thereby into a chromic compound.

The blue solution of chromous chloride may also be obtained by the action of metallic zinc on the green solution of the hydrated chromic chloride. The zinc must be employed in large excess, but if the solution remains for a long time in contact with the zinc the whole of the chromium is converted into chromic oxychloride. Other chromic salts are also reduced by zinc into **chromous salts**, CrX_2 . The reducing power of these salts is very great. From cupric salts they separate cuprous salts, from stannous salts they precipitate metallic tin, and they reduce mercuric salts into mercurous and ferric into ferrous salts. Moreover, they absorb oxygen from the air directly. With potassium chromate they give a brown precipitate of chromium dioxide or of chromic oxide, according to the relative amounts of the substances taken: $\text{CrO}_3 + \text{CrO} = 2\text{CrO}_2$ or $\text{CrO}_3 + 3\text{CrO} = 2\text{Cr}_2\text{O}_3$. Aqueous ammonia gives a blue precipitate, and in the presence of ammoniacal salts a blue liquid is obtained which turns red in the air owing to oxidation. This is accompanied by the formation of compounds analogous to those given by cobalt (Chap. XXII.). A mixture of chromous chloride solution with a hot saturated solution of sodium acetate, $\text{C}_2\text{H}_3\text{NaO}_2$, gives, on cooling, transparent red crystals of chromous acetate, $\text{C}_4\text{H}_6\text{CrO}_4 \cdot \text{H}_2\text{O}$. This salt is also a powerful reducing agent, but may be kept for a long time in a vessel full of carbonic anhydride.

The insoluble anhydrous *chromic chloride* CrCl_3 very easily passes into solution in the presence of a trace (0.004) of *chromous chloride*, CrCl_2 . This remarkable phenomenon was observed by Peligot and explained by Löwel in the following manner: chromous chloride, as a lower stage of oxidation, is capable of absorbing both oxygen and chlorine, combining with various substances. It is able to decompose many chlorides by taking up chlorine from them; thus it precipitates mercurous chloride from a solution of mercuric chloride, and in so doing passes into chromic chloride: $2\text{CrCl}_2 + 2\text{HgCl}_2 = \text{Cr}_2\text{Cl}_6 + 2\text{HgCl}$. Let us suppose that the same phenomenon takes place when the CrCl_3 is mixed with a solution of CrCl_2 . The latter will then take up a portion of the chlorine of the former, and pass into a soluble hydrate of CrCl_3 (hydrochloride of oxide of chromium), and the CrCl_2 will pass into CrCl_3 . The chromous chloride re-formed in this manner will then act on a fresh quantity of the chromic chloride, and so on. This view is confirmed by the fact that other chlorides, capable of absorbing chlorine like chromous chloride, also induce the solution of the insoluble chromic chloride—for example, ferrous chloride, FeCl_2 , and cuprous chloride. The solution of chromic

oxides, by the reduction of chromates (for example, of ammonium or mercuric chromate) and by the decomposition (splitting up) of the saline

chloride in water obtained by these methods is perfectly identical with that formed by dissolving chromic hydroxide in hydrochloric acid. On evaporating the green solution obtained in this manner, it gives a green mass, containing water. On further heating it leaves a soluble chromic oxychloride, and when ignited it first forms an insoluble oxychloride and then chromic oxide; but no anhydrous chromic chloride, Cr_2Cl_6 , is formed by heating the aqueous solution of chromic chloride. At 100° the composition of the green hydrate is $\text{Cr}_2\text{Cl}_6 \cdot 9\text{H}_2\text{O}$, and on evaporation at the ordinary temperature over H_2SO_4 crystals are obtained with 12 equivalents of water; the red mass obtained at 120° has the composition $\text{Cr}_2\text{O}_3 \cdot 4\text{Cr}_2\text{Cl}_6 \cdot 24\text{H}_2\text{O}$. The greater portion of it is soluble in water, like the mass which is formed at 150° . The latter consists of $\text{Cr}_2\text{O}_3 \cdot 2\text{Cr}_2\text{Cl}_6 \cdot 9\text{H}_2\text{O} = 3(\text{Cr}_2\text{OCl}_4 \cdot 3\text{H}_2\text{O})$ —that is, it presents the same composition as chromic chloride in which one atom of oxygen replaces two of chlorine. And if the hydrate of chromic chloride be regarded as $\text{Cr}_2\text{O}_3 \cdot 6\text{HCl}$, the substance which is obtained should be regarded as $\text{Cr}_2\text{O} \cdot 4\text{HCl}$ combined with water, H_2O . The addition of alkalis—for example, baryta—to a solution of chromic chloride immediately produces a precipitate, which, however, re-dissolves on shaking, owing to the formation of one of the oxychlorides just mentioned, which may be regarded as **basic salts**. Thus we may represent the product of the change produced in chromic chloride under the influence of water and heat by the following formulæ: first $\text{Cr}_2\text{O}_3 \cdot 6\text{HCl}$ or $\text{Cr}_2\text{Cl}_6 \cdot 3\text{H}_2\text{O}$ is formed, then $\text{Cr}_2\text{O}_3 \cdot 4\text{HCl} \cdot \text{H}_2\text{O}$ or $\text{Cr}_2\text{OCl}_4 \cdot 3\text{H}_2\text{O}$, and lastly $\text{Cr}_2\text{O}_3 \cdot 2\text{HCl} \cdot 2\text{H}_2\text{O}$ or $\text{Cr}_2\text{O}_2\text{Cl}_2 \cdot 3\text{H}_2\text{O}$. In all three cases there are 2 equivalents of chromium to at least 3 equivalents of water. These compounds are intermediate between chromic hydroxide and chloride.

It is very important, in this connection, to notice two facts: (1) That the whole of the chlorine in the above compounds is not precipitated from their solutions by silver nitrate; thus, the normal salt of the composition $\text{Cr}_2\text{Cl}_6 \cdot 9\text{H}_2\text{O}$ only gives up two-thirds of its chlorine. Therefore Peligot supposes that the normal salt contains the oxychloride combined with hydrochloric acid: $\text{Cr}_2\text{Cl}_6 + 2\text{H}_2\text{O} = \text{Cr}_2\text{O}_2\text{Cl}_2 \cdot 4\text{HCl}$, and that the chlorine held as hydrochloric acid reacts with the silver, whilst that held in the oxychloride does not enter into reaction, just as we observe a very feebly developed faculty for reaction in the anhydrous chromic chloride. (2) If the green aqueous solution of CrCl_3 is left to stand for some time, it ultimately turns violet; in this form the whole of the chlorine is precipitated by AgNO_3 , whilst boiling reconverts it into the green variety. Löwel obtained the violet solution of hydrochloride of chromic oxide by decomposing the violet chromic sulphate with barium chloride. But if the violet solution be boiled, and so converted into the green modification, silver nitrate will then only precipitate a portion of the chlorine.

Recoura (1890–1893) obtained a crystalhydrate of violet chromium sulphate, $\text{Cr}_2(\text{SO}_4)_3$, with 18 or 15 H_2O . By boiling a solution of this crystalhydrate, he converted it into the green salt, which, when treated with alkalis, gave a precipitate of $\text{Cr}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$, soluble in $2\text{H}_2\text{SO}_4$ (and not 3), and only forming the basic salt, $\text{Cr}_2(\text{OH})_2(\text{SO}_4)_2$. He therefore concludes that the green salts are basic salts. The cryoscopic determination made by A. Speransky (1892) and by Marchetti (1892) give a greater 'depression' for the violet than for the green salts, indicating a greater molecular weight for the latter.

Piccini's researches (1894) throw an important light upon the peculiarities of the green CrCl_3 ; he showed (1) that AgF (in contradistinction to the other salts of silver) precipitates all the chlorine from an aqueous solution of the green variety; (2) that solutions of green $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ in ethyl alcohol and acetone precipitate all their chlorine when mixed with a similar solution of AgNO_3 ; (3) that the rise of the boiling-point of the green ethyl alcohol and acetone solutions of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ (Chap. VII., note 27a) shows that i in this case (as in the aqueous solutions of MgSO_4 and HgCl_2) is nearly equal to 1, that is, that they are like solutions of non-conductors; (4) that a solution of green CrCl_3 in methyl alcohol at first precipitates about $\frac{1}{3}$ of its chlorine (an aqueous solution about $\frac{2}{3}$) when treated with AgNO_3 , but after a time the whole of the chlorine is precipi-

compounds of the oxide itself, CrX_3 or Cr_2X_6 , like alumina, which it resembles in forming a feeble base, readily forming double and basic salts, besides neutral CrX_3 . In this respect it is particularly noticeable that the chromic salts can be either violet or green, even when of exactly the same composition, so that the application of heat or other change of conditions converts violet solutions into green, which again gradually become violet at the ordinary temperature. The difference is not limited to colour, but is also seen in the physical and chemical properties. The salts of the violet variety usually crystallise with ease, while the green salts often do not. The former immediately enter into double saline decompositions in which the whole of their haloid participates, while only a portion enters into reaction in the case of the green salts (see notes 7 and 8). Although this remarkable instance of isomerism has formed and is forming the object of research, it still remains unexplained in many relations, and in its essential points recalls the case of phosphoric acid.

Although chromic oxide is not acted on by hydrogen at a high temperature, it is reduced with comparative ease in the form of solutions

tated; and (5) that an aqueous solution of the green variety gradually passes into the violet, while a methyl alcohol solution preserves its green colour, both of itself and also after the whole of the chlorine has been precipitated by AgNO_3 . If, however, in an aqueous or methyl alcoholic solution only a portion of the chlorine is precipitated, the solution gradually turns violet.

The green modification of chromic chloride does not give double salts with the metallic chlorides, whilst the violet variety forms compounds, $\text{Cr}_2\text{Cl}_6 \cdot 2\text{RCl}$ (where R is an alkali metal). As the result of all the existing researches on the green and violet chromic salts, it appears to me most probable that their difference is determined by the feeble basic character of chromic oxide, by its faculty of giving basic salts, and by the colloidal properties of its hydroxide (these three properties are mutually connected), and, moreover, it seems to me that the relation between the green and violet salts of chromic oxide answers best to that between the different hydrates of phosphoric acid (Chap. XIX.) or to the relation of the purpureo- to the luteo-cobaltic salts (Chap. XXII., note 35).

But this leads to problems of another kind, more complex and difficult to understand, owing to the insufficiency of the existing chemical data, and especially on account of the incapacity evinced by the chlorine in salts containing it for reacting with silver salts. This recalls the long known case of the double cyanides such as ferricyanide of potassium, the cyanogen of which does not exhibit any of those reactions (instantaneous) of double decomposition proper to the ordinary cyanides. Although they have been assumed to contain complex radicles, still it is simpler to recognise in them the influence of the association of an aggregation of elements (of multiple and variable valency) which directs the reaction in a different course. The other side of the question is still more complicated. Here we have polymerides, colloidal forms, and cases of isomerism (see Chap. XXII., Fe_2O_3). It seems to me that the recognition of complex radicles (or, what is essentially the same, of special ions) as an explanation of such phenomena does not answer to the true principles of science, for it only gives, I think, a new means of expressing facts, and not of explaining them, and therefore it appears to me that the essence of those differences which are found in the green varieties of the chromic salts is not yet quite clear, and that these substances offer a wide field, like many other branches of our science, for future research.

of its salts, CrX_3 . Such reducing agents as Zn and H_2SO_4 convert them into chromous salts, CrX_2 ; while others, such as sodium amalgam, even reduce it to metallic chromium. The salts of the suboxide, CrX_2 , form blue solutions and themselves act as powerful reducing agents, and even absorb free oxygen.

Metallic chromium was obtained by Deville (probably containing carbon) by reducing chromic oxide with carbon at a temperature near the melting-point of platinum. Chromium (sp. gr. 5.9) has a steel-grey colour, and is very hard, takes a good polish, and dissolves in hydrochloric acid, but cold dilute sulphuric and nitric acids have no action upon it. Bunsen obtained metallic chromium by decomposing a solution of chromic chloride, Cr_2Cl_6 , by a galvanic current, as scales of a grey colour (sp. gr. 7.3). Wöhler obtained crystalline chromium by igniting a mixture of the anhydrous chromic chloride (Cr_2Cl_6 ; note 7a) with finely divided zinc, and sodium and potassium chlorides, at the boiling-point of zinc. When the resultant mass has cooled, the zinc may be dissolved in dilute nitric acid, and grey crystalline chromium (sp. gr. 6.81) is left behind. Frémy also prepared crystalline chromium by the action of the vapour of sodium on anhydrous chromic chloride in a stream of hydrogen. The crystals of metallic chromium were grey cubes having a considerable hardness and withstanding the action of acids. Gladzel (1890) obtained a crystalline powder of Cr by heating the double chloride KCrCl_4 with magnesium. Its sp. gr. was 6.7, and it dissolved readily in acids with the evolution of hydrogen. This seems to indicate a discrepancy between the results of different investigators, which has only been recently explained. Moissan (1893) heated chromic oxide with carbon in the electric furnace, and at first obtained chromium carbide (two carbides are known, Cr_2C and Cr_3C_2 , both extremely hard), and then, after the addition of a fresh amount of Cr_2O_3 , fused metallic chromium of a white colour, malleable and capable of taking a fine polish. Goldschmidt (1900) proposed to obtain fused chromium by heating oxide of chromium with aluminium powder. Metallic chromium (and its alloy with iron) is manufactured on a large scale for steel works, as it endows steel with great hardness. The sp. gr. of the purest chromium is about 6.8. It fuses at $1,800^\circ$. It acts on acids with greater energy the more impurities (apparently Si and Fe) it contains; it evolves hydrogen with HCl, forming CrCl_2 ; but an acid solution of this chromous compound (blue) is easily converted into the chromic compound, CrCl_3 , with the evolution of hydrogen by contact action (platinum black, &c.) (Doring, 1902). However, metallic chromium in the presence of acids at the ordinary temperature or by superficial oxidation as an anode, &c., easily becomes passive and ceases to act on acids; but if

this passive chromium be heated with an acid it again becomes active (Hittorf, 1899), and this accounts for the discrepancy in the first statements respecting the action of acids upon metallic chromium.

Chromium is employed as an ingredient in steel, for 3 per cent. of Cr, and one and a half of C, render steel exceedingly hard. An alloy of iron and chromium is sometimes prepared for this purpose by directly reducing chrome iron ore in the blast furnace.

The two analogues of chromium, **molybdenum** and **tungsten** (or wolfram), are of still rarer occurrence in nature, and form acid oxides, RO_3 , which are still less energetic than CrO_3 .^{8a} Tungsten occurs in the some-

^{8a} The atomic compositions of the tungsten and molybdenum compounds are taken as being identical with that of the compounds of sulphur and chromium, because (1) both these metals give two oxides in which the amounts of oxygen per given amount of metal stand in the ratio 2:3; (2) the higher oxide is of the latter kind, and, like chromic and sulphuric anhydrides, it has an acid character; (3) certain of the molybdates are isomorphous with the sulphates; (4) the specific heat of tungsten is 0.0334, consequently the product of the atomic weight and specific heat is 6.15, like that of the other elements—it is the same with molybdenum, $96.0 \times 0.0722 = 6.9$; (5) tungsten forms with chlorine not only compounds, WCl_6 , WCl_5 , and WOCl_4 , but also WO_2Cl_2 , a volatile substance and the analogue of chromyl chloride, CrO_2Cl_2 , and of sulphuryl chloride, SO_2Cl_2 . Molybdenum gives the chlorine compounds, MoCl_2 , $\text{MoCl}_3(?)$, MoCl_4 (fuses at 194° , boils at 268° ; according to Debray it has the composition MoCl_5), MoOCl_4 , MoO_2Cl_2 , and $\text{MoO}_2(\text{OH})\text{Cl}$. The existence of tungsten hexachloride, WCl_6 , is an excellent proof of the fact that the type SX_6 appears in the analogues of sulphur as in SO_3 ; (6) the vapour density accurately determined for the chlorine compounds, MoCl_4 , WCl_6 , WCl_5 , WOCl_4 (Roscoe), leaves no doubt as to the molecular composition of the compounds of tungsten and molybdenum, for the observed and calculated results entirely agree.

Tungsten is sometimes called 'scheele' in honour of Scheele, who discovered it in 1781, and molybdenum in 1778. Tungsten is also known as 'wolfram'; the former name was the name given to it by Scheele, because he extracted it from the mineral then known as tungsten and now called scheelite, CaWO_4 . The researches of Roscoe, Blomstrand, and others have subsequently thrown considerable light on the whole history of the compounds of molybdenum and tungsten.

The ammonium salts of tungstic and molybdic acids, when ignited, leave the anhydrides, which resemble each other in many respects. **Tungstic anhydride**, WO_3 , is a yellowish substance, which only fuses at a strong heat, and has a sp. gr. of 6.8. It is insoluble both in water and acid, but solutions of the alkalis, and even of the alkali carbonates, dissolve it, especially when heated, forming alkaline salts. **Molybdic anhydride**, MoO_3 , is obtained by igniting the acid (hydrate) or its ammonium salt, and forms a white mass which fuses at a red heat, and solidifies to a yellow crystalline mass of sp. gr. 4.4; whilst on further heating this anhydride **sublimes** in pearly scales—this enables it to be obtained in a tolerably pure state. Water dissolves it in small quantities—1 part requires 600 parts of water for its solution. The hydrates of molybdic anhydride are *soluble also in acids* (a hydrate, H_2MoO_4 , is obtained from the nitric acid solution of the ammonium salt), which forms one of their distinctions from the tungstic acids. But after ignition, molybdic anhydride is insoluble in acids, like tungstic anhydride; alkalis dissolve this anhydride forming molybdates. Potassium bitartrate dissolves the anhydride with the aid of heat. None of the acids yet considered by us form so many different salts with one and the same base (alkali) as do molybdic and tungstic acids. The composition of these salts, and their properties also, vary considerably. The most important discovery in this respect was made by Marguerite and Laurent, who showed that the salts which contain a large proportion of tungstic acid are easily soluble in water,

what rare minerals, scheelite, CaWO_4 , and wolfram, the latter being an isomorphous mixture of the normal tungstates of iron and manganese,

and ascribed this property to the fact that tungstic acid may be obtained in **several states**. The common tungstates, obtained with an excess of alkali, have an alkaline reaction, and on the addition of sulphuric or hydrochloric acid deposit first an acid salt and then a hydrate of tungstic acid, which is insoluble both in water and acids; but if, instead of sulphuric or hydrochloric acid, we add acetic or phosphoric acid, or if the tungstate be saturated with a fresh quantity of tungstic acid, which may be done by boiling the solution of the alkali salt with the precipitated tungstic acid, a solution will be obtained which, on the addition of sulphuric or a similar acid, does not give a precipitate of tungstic acid at the ordinary or at higher temperatures. The solution is then considered to contain salts of a peculiar acid which Laurent, Riche, and others called **metatungstic acid**. Those salts which with acids immediately give the insoluble tungstic acid have the composition R_2WO_4 , RHWO_4 , whilst those which give the soluble metatungstic acid contain a far greater proportion of the acid elements. Scheibler obtained the (soluble) metatungstic acid itself by treating the soluble barium (meta-) tetratungstate, BaO_4WO_3 , with sulphuric acid. Subsequent research showed the existence of a similar phenomenon for molybdic acid. There is no doubt that this is a case of colloidal modifications and of differences like those of the phosphoric acids.

The tungstates and molybdates have been investigated by Marguerite, Laurent, Marignac, Riche, Scheibler, Struve and Svanberg, De la Fontaine, and others. For a given amount of base the salts contain one to eight equivalents of molybdic or tungstic anhydride; i.e., if the base have the composition RO , the highest proportion of base will be contained by the salts of the composition RO_2WO_3 or RO_2MoO_3 —that is, by those salts which correspond with the normal acids H_2WO_4 and H_2MoO_4 of the same nature as sulphuric acid; but there also exist salts of the composition RO_2WO_4 , RO_3WO_3 , . . . RO_8WO_3 . The water contained in the composition of the poly-acid salts is often not taken into account. The properties of the salts holding different proportions of acid oxide vary considerably, but one salt may be converted into another with great facility by the addition of acid or base, and the greater the proportion of the elements of the acid in a salt, the more stable, within a certain limit, is its solution and the salt itself. Muslins, &c., are sometimes treated with a solution of sodium tungstate to render them non-inflammable, for instance, for use on the stage.

The most common **ammonium molybdate** has the composition $(\text{NH}_4\text{HO})_6\text{H}_2\text{O}_7\text{MoO}_3$ (or, according to Marignac and others, NH_4HMoO_4), and is prepared by evaporating an ammoniacal solution of molybdic acid. It is used in the laboratory for precipitating phosphoric acid, and is purified for this purpose by mixing its solution with a small quantity of magnesium nitrate in order to precipitate any phosphoric acid present, filtering, and then adding nitric acid and evaporating to dryness. A pure ammonium molybdate free from phosphoric acid may then be extracted from the residue.

Phosphoric acid forms insoluble compounds with the oxides of uranium, iron, tin, bismuth, &c., having feeble basic and even acid properties. This depends perhaps on the fact that the atoms of hydrogen in phosphoric acid are very varied in character, as we saw above. Those atoms of hydrogen which are replaced with difficulty by ammonium, sodium, &c., are probably easily replaced by feebly energetic acid groups; that is, the formation of particular complex substances may be expected to take place at the expense of these hydrogen atoms of phosphoric acid and of certain feeble metallic acids; and these substances will still be acids, because the hydrogen of the phosphoric acids and metallic acids, which is easily replaced by metals, is not removed by their mutual combination, but remains in the resultant compound. Such a conclusion is verified in the **phosphomolybdic acids** obtained (1888) by Debray. If a solution of ammonium molybdate be acidified, and a small amount of a solution (it may be acid) containing orthophosphoric acid or its salts be added to it so that there are

(MnFe)WO₄. Molybdenum is most frequently met with as molybdenite, MoS₂, which presents a certain resemblance to graphite in its physical

at least 40 parts of molybdic acid present to 1 part of phosphoric acid), then, after a period of twenty-four hours, the whole of the phosphoric acid will be separated as a yellow precipitate, containing, however, not more than 3 to 4 per cent. of phosphoric anhydride, about 3 per cent. of ammonia, about 90 per cent. of molybdic anhydride, and about 4 per cent. of water. The formation of this precipitate is so distinct and so complete that this method is employed for the detection and separation of the smallest quantities of phosphoric acid. Phosphoric acid was found by this means to be present in the majority of rocks. The precipitate is soluble in ammonia and its salts, in alkalies and phosphates, but is perfectly insoluble in nitric, sulphuric, and hydrochloric acids in the presence of ammonium molybdate. The composition of the precipitate appears to vary under the conditions of its precipitation, but its nature became clear when the acid corresponding with it was obtained. If the above-described yellow precipitate is boiled in aqua regia, the ammonia is destroyed, and an acid is obtained in solution, which when evaporated in the air crystallises out in yellow oblique prisms of approximately the composition, P₂O₅, 20MoO₃, 26H₂O (generally considered to consist of H₃PO₄, 12H₂MoO₄ = P₂O₅, 24MoO₃, 27H₂O; most probably the amount of MoO₃ is variable). Such an unusual proportion of component parts is explained by the above-mentioned considerations. We saw above that molybdic acid readily gives salts R₂O, *n*MoO₃, *m*H₂O, which we may imagine to correspond to a hydrate MoO₂(HO)₂, *n*MoO₃, *m*H₂O. And we may suppose that such a hydrate reacts on orthophosphoric acid, forming water and compounds of the composition MoO₂(HPO₄)₂, *n*MoO₃, *m*H₂O or MoO₂(H₂PO₄)₂, *n*MoO₃, *m*H₂O; this is actually the composition of phosphomolybdic acid. Probably it contains a portion of the hydrogen, replaceable by metals, of both the acids H₃PO₄ and of H₂MoO₄. The crystalline acid above is probably H₃MoPO₇, 9MoO₃, 12H₂O. This acid is really tribasic, because its aqueous solution precipitates salts of potassium, ammonium, rubidium (but not lithium and sodium) *from acid solutions*, and gives a *yellow* precipitate of the composition R₃MoPO₇, 9MoO₃, 8H₂O, where R = NH₄, or K. Besides these, salts of another composition may be obtained, as would be expected from the preceding. These salts are only stable in acid solutions (which is naturally due to their containing an excess of acid oxides), whilst under the action of alkalies they give *colourless* phosphomolybdates of the composition R₃MoPO₇, MoO₃, 3H₂O. The corresponding salts of potassium, silver, and ammonium, are easily soluble in water and crystalline.

Phosphomolybdic acid is an example of the **complex inorganic acids** first obtained by Marignac and afterwards generalised and studied in detail by Gibbs. We shall afterwards meet with several examples of such acids, and we will now call attention to the fact that they are usually formed by weak polybasic acids (boric, silicic, molybdic, &c.), and in certain respects resemble the cobaltic and similar complex compounds with which we shall become acquainted in the following chapter. As an example, we may mention certain complex compounds containing molybdic and tungstic acids. The action of ammonium molybdate upon a dilute solution of purpureo-cobaltic salts (see Chap. XXII.) acidulated with acetic acid gives a salt which, after drying at 100° has the composition Co₂O₃, 10NH₃, 7MoO₃, 3H₂O. After ignition this salt leaves a residue having the composition 2CoO, 7MoO₃. An analogous compound is also obtained for tungstic acid, having the composition Co₂O₃, 10NH₃, 10WO₃, 9H₂O. In this case, after ignition there remains a salt of the composition CoO, 5WO₃ (Carnot, 1889). Professor Kurnakoff (1889), by treating a solution of potassium and sodium molybdates containing suboxide of cobalt, CoO, with bromine, obtained salts of the oxide Co₂O₃ having the composition: 3K₂O, Co₂O₃, 12MoO₃, 20H₂O (light-green) and 3K₂O, Co₂O₃, 10MoO₃, 10H₂O (dark-green). Péchard (1893) obtained salts of the four complex phosphotungstic acids by evaporating equivalent mixtures of solutions of phosphoric and metatungstic acids: phosphotrimetatungstic acid, P₂O₅, 12WO₃, 18H₂O, phosphotetrametatungstic acid, P₂O₅, 16WO₃, 69H₂O, phosphopentametatumgstic acid, P₂O₅, 20WO₃, H₂O, &c. Kehrman (1892) considers the possibility of obtaining an unlimited number of such salts to

properties and softness. It also occurs, but much more rarely, as a yellow lead ore, PbMoO_4 . In both these forms molybdenum occurs in

be a general characteristic of such compounds. Mahom and Friedheim (1892) obtained compounds of similar complexity for molybdc and arsenic acids.

Normal sodium tungstate, Na_2WO_4 , is obtained by heating a strong solution of sodium carbonate with tungstic acid to a temperature of 80° ; if the solution is filtered hot, it crystallises in rhombic tabular crystals, having the composition $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, which remain unchanged in the air and are easily soluble in water. When this salt is fused with a fresh quantity of tungstic acid, it gives a ditungstate, which is soluble in water and separates from its solution in crystals containing water. The same salt is obtained by carefully adding hydrochloric acid to the solution of the normal salt so long as a precipitate does not appear, and the liquid still has an alkaline reaction. This salt has the composition (at 100°) $\text{Na}_6\text{W}_8\text{O}_{24} \cdot 16\text{H}_2\text{O}$ —that is, it corresponds with the similar salt of molybdc acid.

If this salt is heated to a red heat in a stream of hydrogen, it loses a portion of its oxygen, acquires a metallic lustre, and turns a golden-yellow colour, and, after being treated with water, alkali, and acid, leaves golden-yellow leaflets and cubes which are very like gold. This very remarkable substance, discovered by Wöhler, has, according to Malaguti's analysis, the composition $\text{Na}_2\text{W}_3\text{O}_9$; that is, it consists, as it were, of a double tungstate of tungsten oxide, WO_2 , and of sodium, $\text{Na}_2\text{WO}_4 \cdot \text{WO}_2 \cdot \text{WO}_2$. With potassium, only one compound is formed (according to Knorre and Schäfer, 1902), of the composition $\text{K}_2\text{W}_4\text{O}_{12}$, whilst sodium gives compounds of varying composition, but all possessing the properties of *tungsten bronzes*, the most remarkable of these being the power of conducting a current like metals. The decomposition of the fused sodium salt is best effected by finely divided tin. This substance has a sp. gr. 6.6; it conducts electricity like metals, and like them has a metallic lustre. When brought into contact with zinc and sulphuric acid it disengages hydrogen, and becomes covered with a coating of copper in a solution of copper sulphate in the presence of zinc—that is, notwithstanding its complex composition it presents to a certain extent the appearance and reactions of the metals. It is not acted on by aqua regia or alkaline solutions, but is oxidised when ignited in air.

The ditungstate mentioned above, deprived of water (having undergone a modification similar to that of metaphosphoric acid), after being treated with water, leaves an anhydrous, sparingly soluble tetratungstate, $\text{Na}_2\text{WO}_4 \cdot 3\text{WO}_3$, which, when heated at 120° in a closed tube with water, passes into an easily soluble metatungstate. It may therefore be said that the metatungstates are hydrated compounds. On boiling solutions of the above-mentioned salts of sodium with the yellow hydrate of tungstic acid, they give a solution of metatungstate, which is the hydrated tetratungstate. Its crystals have the composition $\text{Na}_2\text{W}_4\text{O}_{13} \cdot 10\text{H}_2\text{O}$. After the hydrate of tungstic acid has stood a long time in contact with a solution of sodium tungstate, it gives a solution which is not precipitated by hydrochloric acid; this must be filtered and evaporated over sulphuric acid in a desiccator (it is decomposed by boiling). It first forms a very dense solution (aluminium floats in it) of sp. gr. 3.0, and octahedral crystals of **sodium metatungstate**, $\text{Na}_2\text{W}_4\text{O}_{13} \cdot 10\text{H}_2\text{O}$, of sp. gr. 3.85, then separate. It effloresces and loses water, and at 100° only two out of the ten equivalents of water remain, but the properties of the salt remain unaltered. If the salt is deprived of water by further heating, it becomes insoluble. At the ordinary temperature one part of water dissolves ten parts of the metatungstate. The other metatungstates are easily obtained from this salt. Thus a strong and hot solution, mixed with a similar one of barium chloride, gives, on cooling, crystals of **barium metatungstate**, $\text{BaW}_4\text{O}_{15} \cdot 9\text{H}_2\text{O}$. These crystals are dissolved without change in water containing hydrochloric acid, and also in hot water, but they are partially decomposed by cold water, with the formation of a solution of metatungstic acid and of the normal barium salt, BaWO_4 .

It is noticeable that a mixture of a solution of tungstic acid with a solution of silicic acid does not coagulate when heated, although the silicic acid alone would do so; this is

the primary rocks, in granites, gneiss, &c., and in iron and copper ores in Saxony, Sweden, and Finland. Tungsten ores are sometimes met-

due to the formation of a **silicotungstic acid**, discovered by Marignac, which presents a fresh example of a complex acid. A solution of a tungstate dissolves gelatinous silica just as it does gelatinous tungstic acid, and when evaporated deposits a crystalline salt of silicotungstic acid. This solution is not precipitated either by acids (a clear analogy to the metatungstates) or by sulphuretted hydrogen, and corresponds with a series of salts. These salts contain one equivalent of silica and 8 equivalents of hydrogen or metals, in the same form as in salts, to 12 or 10 equivalents of tungstic anhydride; for example, the crystalline potassium salt has the composition $K_8W_{12}SiO_{42}, 14H_2O = 4K_2O, 12WO_3, SiO_2, 14H_2O$. Acid salts are also known in which half of the metal is replaced by hydrogen. Friedheim and Henderson obtained compounds of still greater complexity, for instance, crystals of a salt $(NH_4)_6SiV_2W_{10}O_{40}, 21H_2O$ and $(NH_4)_6SiV_2W_9O_{37}, 24H_2O$ (both contain in all 61 atoms of oxygen). The complexity of the composition of such complex acids (for example, of phosphomolybdic acid) involuntarily leads to the idea of polymerisation, which must be recognised for silica, lead oxide, and other compounds. This polymerisation, it seems to me, may be understood thus: a hydrate A (for example, tungstic acid) is capable of combining with a hydrate B (for example, silicic or phosphoric acid, with or without the disengagement of water), and by reason of this faculty it is capable of polymerisation—that is, A combines with A—combines with itself—just as aldehyde, C_2H_4O , or the cyanogen compounds are able to combine with hydrogen, oxygen, &c., and are liable to polymerisation. According to this view, the molecule of tungstic anhydride is probably much more complex than it is generally represented. Such a view also finds a certain confirmation in the researches made by Graham on the colloidal state of tungstic acid, because colloidal properties only appertain to compounds of a very complex composition. When sodium tungstate, mixed in dilute solution with an equivalent quantity of dilute hydrochloric acid, is placed in a dialyser, hydrochloric acid and sodium chloride pass through the membrane, and a solution of tungstic acid remains. The solution has a bitter, astringent taste, and does not yield gelatinous tungstic acid (hydrogel), either when heated or on the addition of acids or salts. It may also be evaporated to dryness; it then forms a vitreous mass of the **hydrosol of tungstic acid**, which adheres strongly to the walls of the vessel in which it has been evaporated, and is perfectly soluble in water. It does not even lose its solubility after having been heated to 200° . Its solution in a small quantity of water forms a gluey mass, just like gum arabic, which is one of the representatives of the hydrosols of colloidal substances. The solution, containing 5 per cent. of the anhydride, has a sp. gr. of 1.047; with 20 per cent., of 1.217; with 50 per cent., of 1.80; and with 80 per cent., of 3.24. The presence of a polymerised trioxide in the form of hydrate, H_2O, W_3O_9 or $H_2O, 4WO_3$, must then be recognised in the solution: this is confirmed by Sabanéeff's cryoscopic determinations (1889). A similar stable solution of molybdic acid is obtained by the dialysis of a mixture of a strong solution of sodium molybdate with hydrochloric acid (the precipitate which is formed is re-dissolved). The addition of alkali to the solutions of the hydrosols of tungstic and molybdic acids immediately results in the re-formation of the ordinary tungstates and molybdates. There appears to be no doubt but that the same transformation is accomplished in the passage of the ordinary tungstates into the metatungstates as takes place in the passage of tungstic acid itself from an insoluble into a soluble state; but this may be even actually proved to be the case, because Scheibler obtained a solution of tungstic acid, before Graham, by decomposing barium metatungstate ($BaO, 4WO_3, 9H_2O$) with sulphuric acid. By treating this salt with sulphuric acid in the amount required for the precipitation of the baryta, Scheibler obtained a solution of metatungstic acid having specific gravities corresponding with those found by Graham.

Péchar'd found that as much heat is evolved by neutralising metatungstic acid as with sulphuric acid.

Questions connected with the metamorphoses or modifications of tungstic and

with in considerable masses in the primary rocks of Bohemia and Saxony, and also in England, America, and the Urals. The preliminary treatment of the ore is very simple; for example, the sulphide, MoS_2 , is roasted, and thus converted into sulphurous anhydride and molybdic anhydride, MoO_3 , which is then dissolved in alkalies, generally in ammonia. The ammonium molybdate is then treated with acids, when the sparingly soluble molybdic acid is precipitated. Tungsten is treated in a different manner. Most frequently the finely ground ore is repeatedly boiled with hydrochloric and nitric acids, and the resultant solutions (of salts of manganese and iron) poured off, until the dark brown mass of ore disappears, whilst the tungstic acid remains, mixed with silica, as an insoluble residue; it is treated also with ammonia, and is thus converted into soluble ammonium tungstate, which passes into solution and yields tungstic acid when treated with acids. This hydrate is then ignited, and leaves tungstic anhydride. The general character of molybdic and tungstic anhydrides is analogous to that of chromic anhydride; they are anhydrides of a feebly acid character, which easily give polyacid salts and colloidal solutions, and, by reduction of the acids, the lower degrees of oxidation, Mo_2O_3 , MoO_2 , and WO_2 .

Hydrogen reduces molybdic and tungstic anhydrides at a red heat. The metals are obtained, like Cr, by means of carbon in the electric furnace or with aluminium. Tungsten is used, like chromium, to give hardness, &c., to an alloy. **Both metals** are infusible, and under the action of heat form compounds with carbon and iron (the addition of tungsten to steel renders the latter ductile and hard).⁹ Molybdenum forms a grey powder, which scarcely aggregates under the most powerful heat, and has a specific gravity of 9.0. It is not acted on by the air at the ordinary temperature, but when ignited it is first converted into a brown, and then into a blue oxide, and lastly into molybdic anhydride. Acids do not act on it—that is, it does not liberate hydrogen from them, not even from hydrochloric acid—but strong sulphuric acid, with the aid of heat, disengages sulphurous anhydride, forming a brown mass, containing a lower oxide of molybdenum. Alkalies in solution

molybdic acids, and the polymerisation and colloidal state of substances, as well as the formation of complex acids, belong to that class of problems the solution of which will do much towards attaining a true comprehension of the mechanism of a number of chemical reactions. I think, moreover, that questions of this kind stand in intimate connection with the theory of the formation of solutions and alloys and other so-called indefinite compounds.

⁹ Moissan (1893) studied the compounds of Mo and W formed with carbon in the electric furnace (they are extremely hard) from a mixture of the anhydrides and carbon. Poleck and Grützner obtained definite compounds, FeW_2 and FeW_2C_3 , for tungsten. Metallic W and Mo displace Ag from its solutions, but not Pb.

do not act on molybdenum, but when fused with it hydrogen is given off; which shows, as does its whole character, the acid properties of the metal. The properties of tungsten are almost identical; it is infusible, has an iron-grey colour, is exceedingly hard, so that it even scratches glass. Its specific gravity is 19.1 (according to Roscoe), or 18.7 (according to Moissan), so that, like uranium, platinum, &c., it is one of the heaviest metals.^{9a} Just as sulphur and chromium have their corresponding persulphuric and perchromic acids, $\text{H}_2\text{S}_2\text{O}_8$ and $\text{H}_2\text{Cr}_2\text{O}_8$, having the properties of peroxides, and corresponding to peroxide of hydrogen, so also molybdenum and tungsten are known to give **permolybdic** and **pertungstic** acids, $\text{H}_2\text{Mo}_2\text{O}_8$ and $\text{H}_2\text{W}_2\text{O}_8$, which have the properties of true peroxides, i.e., they easily disengage iodine from KI and chlorine from HCl, easily part with their oxygen, and are formed by the action of peroxide of hydrogen, into which they are readily reconverted.^{9b}

^{9a} Tungsten and molybdenum form sulphides having an acid character, like carbon bisulphide or stannic sulphide. If sulphuretted hydrogen is passed through a solution of a molybdate it does not give a precipitate unless sulphuric acid is present, when a dark-brown precipitate of **molybdenum trisulphide**, MoS_3 , is formed. When this sulphide is ignited without access of air it gives the bisulphide MoS_2 ; the latter is not able to combine with potassium sulphide like the trisulphide MoS_3 , which forms a salt, K_2MoS_4 , corresponding with K_2MoO_4 . This is soluble in water, and separates out from its solution in red crystals, which have a metallic lustre and reflect a green light. It is easily obtained by heating the native bisulphide, MoS_2 , with potash, sulphur, and a small amount of charcoal, which serves for deoxidising the oxygen compounds. Tungsten gives similar compounds, R_2WS_4 , where $\text{R} = \text{NH}_4, \text{K}, \text{Na}$. They are decomposed by acids, with the separation of tungsten trisulphide, WS_3 , and molybdenum trisulphide, MoS_3 . Rideal (1892) obtained W_2N_3 by heating WO_3 in NH_3 . This compound exhibited the general properties of metallic nitrides.

^{9b} They may be regarded as compounds of H_2O_2 with 2MoO_3 and 2WO_3 , &c. Their formation (Boerwald, 1884; Kemmerer, 1891) is at once seen in the coloration (not destroyed by boiling), which is obtained on mixing a solution of the salts with peroxide of hydrogen, and on treating, for instance, molybdic acid with a solution of peroxide of hydrogen (Péchar, 1892). The acid then forms an orange-coloured solution, which after evaporation *in vacuo* leaves $\text{Mo}_2\text{H}_2\text{O}_8, 4\text{H}_2\text{O}$ as a crystalline powder, and loses $4\text{H}_2\text{O}$ at 100° , above which it decomposes with the evolution of oxygen. When peroxide of hydrogen acts upon a solution of potassium molybdate, well-formed yellow crystals belonging to the triclinic system separate out in the cold. When these crystals are heated *in vacuo* they first lose water and then decompose, leaving a residue composed of the salt originally taken. They are soluble in water but insoluble in alcohol. Their composition is represented by the formula $\text{K}_2\text{Mo}_2\text{O}_8, 2\text{H}_2\text{O}$. A corresponding sodium pertungstate has been obtained by Péchar by boiling sodium tungstate with a solution of peroxide of hydrogen for several minutes. The solution rapidly turns yellow, and no longer gives a precipitate of tungstic acid when treated with nitric acid. When evaporated *in vacuo* the solution leaves a thick syrupy liquid from which stellate crystals separate out; these crystals are more soluble in water than the salt originally taken. Their composition answers to the formula $\text{Na}_2\text{W}_2\text{O}_8, 2\text{H}_2\text{O}$. When treated with oxygen acids they give peroxide of hydrogen, and disengage chlorine and iodine from hydrochloric acid and potassium iodide.

Piccini (1891) showed that peroxide of hydrogen not only combines with the oxygen

Uranium, $U=239$, has the highest atomic weight of all the analogues of chromium, and indeed of all the elements yet known. Its highest salt-forming oxide, UO_3 , shows very feeble acid properties. Although it gives sparingly soluble yellow compounds with alkalis, which fully correspond with the dichromates—for example, $Na_2U_2O_7 = Na_2O, 2UO_3$ ¹⁰—yet it more frequently and easily reacts with acids,

compounds of Mo and W, but also with their fluo-compounds, among which ammonium fluo-molybdate, $MoO_2F_2, 2NH_4$, and others have long been known. The action of peroxide of hydrogen upon these compounds gives salts containing a larger amount of oxygen; for instance, a solution of $MoO_2F_2, 2KF, H_2O$ with peroxide of hydrogen gives a yellow solution which after cooling deposits yellow crystalline flakes of $MoO_3F_2, 2KF, H_2O$, resembling in their external appearance the salt originally taken.

If permolybdic acid be regarded as $2MoO_3 + H_2O_2$, i.e., as containing the elements of peroxide of hydrogen, then Piccini's compound will also be found to contain the original salts + H_2O_2 ; for example, from $MoO_2F_2, 2KF, H_2O$ there is obtained a compound $MoO_2F_2, 2KF, H_2O_2$, i.e., instead of H_2O they contain H_2O_2 . The capacity of the salts of molybdenum and tungsten to retain a further amount of oxygen or H_2O_2 probably bears some relation to their property of giving complex acids and of polymerising, which has been considered in note 8a.

¹⁰ Uranium trioxide, or uranic oxide, shows its feeble basic and acid properties in many respects. (1) Solutions of uranic salts give yellow precipitates with alkalis, but these precipitates do not contain the hydrate, but compounds of it with bases; for example, $2UO_2(NO_3)_2 + 6KHO = 4KNO_3 + 3H_2O + K_2U_2O_7$. There are other **urano-alkali compounds** of the same constitution; for example, $(NH_4)_2U_2O_7$ (known commercially as uranic oxide), MgU_2O_7, BaU_2O_7 . They are the analogues of the dichromates. Sodium uranate is the most generally used under the name of uranium yellow, $Na_2U_2O_7$. It is used for imparting the characteristic yellow-green tint to glass and porcelain. Neither heat nor water nor feeble acids are able to extract the alkali from sodium uranate, $Na_2U_2O_7$, and therefore it is a true insoluble salt, of a yellow colour, and clearly indicates the acid character (although feeble) of uranic oxide. (2) The carbonates of the alkaline earths (for instance, barium carbonate) precipitate uranic oxide from its salts, as they do all the salts of feeble bases, for example, R_2O_3 . (3) The **alkaline carbonates**, when added to solutions of uranic salts, give a **precipitate, which is soluble in an excess of the reagent**, and particularly so if the acid carbonates are taken. This is due to the fact that (4) the uranyl salts **easily form double salts** with the salts of the alkali metals, including those of ammonium. Uranium, in the form of these double salts, often gives salts of well-defined crystalline form, although the simple salts are little prone to appear in crystals. Such, for example, are the salts obtained by dissolving potassium uranate, $K_2U_2O_7$, in acids, with the addition of potassium salts of the same acids. Thus, with hydrochloric acid and potassium chloride a well-formed crystalline salt, $K_2(UO_2)Cl_4, 2H_2O$, belonging to the monoclinic system, is produced. This salt decomposes in dissolving in pure water. Among these double salts we may mention the double carbonate with the alkalies, $R_4(UO_2)(CO_3)_3$ (equal to $2R_2CO_3 + UO_2CO_3$); the acetates, $R(UO_2)(C_2H_3O_2)_3$, for instance, the sodium salt, $Na(UO_2)(C_2H_3O_2)_3$, and the potassium salt, $K(UO_2)(C_2H_3O_2)_3, H_2O$; the sulphates, $R_2(UO_2)(SO_4)_3, 2H_2O$, &c. In the preceding formula $R=K, Na, NH_4$, or $R_2=Mg, Ba$, &c. *This property of giving comparatively stable double salts indicates feebly developed basic properties*, because double salts are mainly formed by salts of distinctly basic metals (these form, as it were, the basic element of a double salt) and salts of feebly energetic bases (these form the acid element of a double salt). For this reason barium does not give double salts with alkalis as magnesium does, and this is why double salts are more easily formed by potassium than by lithium in the series of the alkali metals. (5) The most remarkable property, proving the feeble energy of uranic oxide as a base, is seen in the fact that

HX, forming fluorescent yellowish-green salts of the composition UO_2X_2 , and in this respect uranic trioxide, UO_3 , differs from chromic anhydride, CrO_3 , although the latter is able to give the oxychloride, CrO_2Cl_2 . In molybdenum and tungsten, however, we see a clear transition from chromium to uranium. Thus, for example, chromyl chloride, CrO_2Cl_2 , is a brown liquid, which volatilises without change and is completely decomposed by water; molybdenum oxychloride, MoO_2Cl_2 , is a crystalline substance of a yellow colour, volatile and soluble in water (Blomstrand), like many salts. Tungsten oxychloride, WO_2Cl_2 , stands still nearer to uranyl chloride in its properties; it forms yellow scales on which water and alkalies act, as they do on many salts (zinc chloride, ferric chloride, aluminium chloride, stannic chloride, &c.), and corresponds perfectly with the difficultly volatile salt, UO_2Cl_2 (obtained by Peligot by the action of chlorine on ignited uranium dioxide, UO_2), which is also yellow and gives a yellow solution with water, like all the salts UO_2X_2 . The property of uranic oxide, UO_3 , of forming salts, UO_2X_2 , is shown in the fact that the hydrated oxide of uranium, $\text{UO}_2(\text{HO})_2$, which is obtained from the nitrate, carbonate, and other salts by the loss of the elements of the acid, is easily soluble in acids, as well as in the fact that the lower grades of oxidation of uranium are able, when treated with nitric acid, to form an easily crystallisable uranyl nitrate, $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$; this is the most commonly occurring uranium salt.¹¹

when their composition is compared with that of other salts those of uranic oxide **always appear as basic salts**. It is well known that a normal salt, R_2X_6 , corresponds with the oxide R_2O_3 , where $\text{X} = \text{Cl}, \text{NO}_3$, &c., or $\text{X}_2 = \text{SO}_4, \text{CO}_3$, &c.; but there also exist basic salts of the same type, where $\text{X} = \text{HO}$ or $\text{X}_2 = \text{O}$. We saw salts of all kinds among the salts of aluminium, chromium, and others. With uranic oxide no salts are known of the types UX_6 , $[\text{UCl}_6]$, $\text{U}(\text{SO}_4)_3$, alums, &c., are not known], nor even salts, $\text{U}(\text{HO})_4\text{X}_2$ or UOX_4 , but it always forms salts of the type $\text{U}(\text{HO})_4\text{X}_2$ or UO_2X_2 . Judging from the fact that nearly all the salts of uranic oxide retain water in crystallising from their solutions, and that this water is difficult to separate from them, it may be thought to be water of hydration. This is seen in part from the fact that the composition of many of the salts of uranic oxide may then be expressed without the presence of water of crystallisation; for instance, $\text{U}(\text{HO})_4\text{K}_2\text{Cl}_4$ (and the salt of NH_4), $\text{U}(\text{HO})_4\text{K}_2(\text{SO}_4)_2$; $\text{U}(\text{HO})_4(\text{C}_2\text{H}_3\text{O}_2)_2$. Sodium uranyl acetate, however, does not contain water.

¹¹ **Uranyl nitrate**, or uranium nitrate, $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, crystallises from its solutions in transparent yellowish-green prisms (from an acid solution), or in tabular crystals (from a neutral solution), which effloresce in the air and are easily soluble in water, alcohol, and ether, have a sp. gr. of 2·8, and fuse when heated, losing nitric acid and water in the process. If the salt itself (Berzelius) or its alcoholic solution (Malaguti) is heated up to the temperature at which oxides of nitrogen are evolved, there then remains a mass which, after being evaporated with water, leaves uranyl hydroxide, $\text{UO}_2(\text{HO})_2$ (sp. gr. 5·93), whilst if the salt is ignited there remains UO_3 , as a brick-red powder, which on further heating loses oxygen and forms the dark-olive uranoso-uranic oxide, U_3O_8 . The solution of the nitrate obtained from the ore is purified in the following manner: Sulphurous anhydride is first passed through it in order to reduce the arsenic acid present into arsenious acid; the solution is then heated to 60°, and sulphuretted

Uranium, which gives an oxide, UO_3 , and the corresponding salt, UO_2X_2 , and dioxide, UO_2 , to which the salts UX_4 correspond, is rarely met with in nature. Uranite or the double orthophosphate of uranic oxide, $\text{R}(\text{UO}_2)_2\text{H}_2\text{P}_2\text{O}_8 \cdot 7\text{H}_2\text{O}$, where $\text{R} = \text{Cu}$ or Ca , uranium-vitriol, $\text{U}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$, samarskite, and æschynite, are very rarely found, and then only in small quantities. Of more frequent and abundant occurrence is the non-crystalline earthy brown uranium ore known as **pitchblende** (sp. gr. 7.2), which is mainly composed of the intermediate oxide, $\text{U}_3\text{O}_8 = \text{UO}_2 \cdot 2\text{UO}_3$. This ore is found at Joachimsthal (in Bohemia) and in Cornwall. It usually contains a number of different impurities, chiefly sulphides and arsenides of lead and iron, as well as lime and silica compounds. In order to expel the arsenic and sulphur, it is roasted, ground, washed with dilute hydrochloric acid, which does not dissolve the uranoso-uranic oxide, U_3O_8 , and the residue is dissolved in nitric acid, which transforms the uranium oxide into the nitrate, $\text{UO}_2(\text{NO}_3)_2$.

It must be observed that the oxide of uranium, first distinguished by Klaproth (1789), was for a long time regarded as able to give metallic uranium under the action of charcoal and other reducing agents (with the aid of heat). But the substance thus obtained was only the **uranium dioxide**, UO_2 . The compound nature of this dioxide,¹² or the

hydrogen passed through it; this precipitates the lead, arsenic, and tin, and certain other metals. This liquid is then filtered and evaporated with nitric acid to crystallisation, and the crystals are dissolved in ether. Or else the solution is first treated with chlorine in order to convert the ferrous chloride (produced by the action of the hydrogen sulphide) into ferric chloride, the oxides are then precipitated by ammonia, and the resultant precipitate, containing the oxides Fe_2O_3 , UO_3 , and compounds of the latter with potash, lime, ammonia, and other bases present in the solution (the latter being due to the property of uranic oxide of combining with bases), is washed and dissolved in a strong, slightly heated solution of ammonium carbonate, which dissolves the uranic oxide, but not the ferric oxide. The solution is filtered, and on cooling deposits a well-crystallising **uranyl ammonium carbonate**, $\text{UO}_2(\text{NH}_4)_4(\text{CO}_3)_3$, in brilliant monoclinic crystals which on exposure to air slowly give off water, carbonic anhydride, and ammonia; the same decomposition is readily effected at 300° , the residue then consisting of uranic oxide. This salt is not very soluble in water, but is readily so in ammonium carbonate; it is obvious that it may readily be converted into all the other salts of oxides of uranium. Uranium salts are also purified in the form of *acetate*, which is very sparingly soluble, or as *oxalate*, which is very difficultly soluble, and is therefore directly precipitated from a strong solution of the nitrate by mixing it with oxalic acid.

We may also mention the **uranyl phosphate**, H_2UPO_6 , which must be regarded as an orthophosphate in which two hydrogens are replaced by the radicle uranyl, UO_2 , i.e., as $\text{H}(\text{UO}_2)\text{PO}_4$. This salt is formed as a hydrated gelatinous yellow precipitate, on mixing a solution of uranyl nitrate with disodium phosphate.

¹² Uranium dioxide, or **uranyl**, UO_2 , which is contained in the salts UO_2X_2 , has the appearance and many of the properties of a metal. Uranic oxide may be regarded as uranyl oxide, $(\text{UO}_2)_2\text{O}$, and its salts as salts of this uranyl; its hydroxide, $(\text{UO}_2)_2\text{H}_2\text{O}_2$, is constituted like CaH_2O_2 . The green oxide of uranium, uranoso-uranic oxide (easily formed from uranic salts by the loss of oxygen), $\text{U}_3\text{O}_8 = \text{UO}_2 \cdot 2\text{UO}_3$, when heated with

presence of oxygen in it, was demonstrated by Peligot (1841) by igniting it with charcoal in a stream of chlorine. He thus obtained the corresponding volatile **uranium tetrachloride**, UCl_4 ,¹³ which, when heated with sodium, gave **metallic uranium** as a grey metal, having a specific gravity of 18.7,¹⁴ and liberating hydrogen from acids, with the

charcoal or hydrogen (dry) gives a brilliant crystalline UO_2 of sp. gr. about 11.0 (Urlaub), which has an appearance resembling that of metals, and decomposes steam at a red heat with the evolution of hydrogen; it does not, however, decompose hydrochloric or sulphuric acid, but is oxidised by nitric acid. The same substance (i.e., uranium dioxide, UO_2) is also obtained by igniting the compound $(\text{UO}_2)\text{K}_2\text{Cl}_4$ in a stream of hydrogen, according to the equation, $\text{UO}_2\text{K}_2\text{Cl}_4 + \text{H}_2 = \text{UO}_2 + 2\text{HCl} + 2\text{KCl}$. It was at first regarded as the metal. In 1841 Peligot found that it contained oxygen, because carbonic oxide and anhydride were evolved when it was ignited with charcoal in a stream of chlorine, and from 272 parts of the substance which was considered to be metal he obtained 382 parts of a volatile product containing 142 parts of chlorine. From this it was concluded that the substance taken contained an equivalent amount of oxygen. As 142 parts of chlorine correspond with 32 parts of oxygen, it followed that $272 - 32 = 240$ parts of metal were combined in the substance with 32 parts of oxygen, and also in the chlorine compound obtained with 142 parts of chlorine. These calculations have been made for the now accepted atomic weight of uranium.

¹³ **Uranium tetrachloride**, uranous chloride, UCl_4 , corresponds with uranous oxide, UO_2 , as a base. It was obtained by Peligot by igniting uranic oxide mixed with charcoal in a stream of *dry* chlorine: $\text{UO}_3 + 3\text{C} + 2\text{Cl}_2 = \text{UCl}_4 + 3\text{CO}$. This green volatile compound (note 12) crystallises in regular octahedra, is very hygroscopic, easily soluble in water with the development of a considerable amount of heat, and no longer separates out from its solution in an anhydrous state, but disengages hydrochloric acid when evaporated. The solution of uranous chloride in water is green. It is also formed by the action of zinc and copper (forming cuprous chloride) on a solution of uranyl chloride, UO_2Cl_2 , especially in the presence of hydrochloric acid and sal-ammoniac. Solutions of uranyl salts are converted into uranous salts by the action of various reducing agents, and among others by organic substances or by the action of light, whilst the salts UX_4 are converted into uranyl salts, UO_2X_2 , by exposure to air or by oxidising agents. Solutions of the green uranyl salts act as powerful reducing agents, and give a brown precipitate of the uranous hydroxide, UH_3O_4 , with potash and other alkalis. This hydroxide is easily soluble in acids but not in alkalis. On ignition it does not form the oxide UO_2 , because it decomposes water, but when the higher oxides of uranium are ignited in a stream of hydrogen or with charcoal they yield uranous oxide. Both it and the chloride UCl_4 dissolve in strong sulphuric acid, forming a green salt, $\text{U}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$. The same salt, together with uranyl sulphate, $\text{UO}_2(\text{SO}_4)$, is formed when the green oxide, U_3O_8 , is dissolved in hot sulphuric acid. The salts obtained in the latter instance may be separated by adding alcohol to the solution, which is left exposed to the light; the alcohol reduces the uranyl salt to uranous salt, an excess of acid being required. An excess of water decomposes this salt, forming a basic salt, which is also easily produced under other circumstances, and consists of $\text{UO}(\text{SO}_4) \cdot 2\text{H}_2\text{O}$ (which corresponds to the uranic salt). According to Orloff (1902), green crystals of $\text{U}(\text{SO}_4)_2 \cdot 8\text{H}_2\text{O}$, previously obtained by Rammelsberg, are formed if an alcoholic or acidulated (with H_2SO_4) solution of UO_2SO_4 is exposed to the sun's rays (reduction takes place). Concerning the peroxide of uranium or peruranic anhydride, UO_4 , see Chap. XX., note 66.

¹⁴ The atomic weight of uranium was formerly taken as half the present one, $\text{U} = 120$, and the oxides U_2O_3 , suboxide UO , and green oxide U_3O_4 , were of the same types as the oxides of iron. With a remote resemblance to the elements of the iron group, uranium presents many points of distinction which do not permit its being grouped with them.

The alteration or doubling of the atomic weight of uranium—i.e., the recognition of $\text{U} = 240$ —was made for the first time in the first (Russian) edition of this work (1871), on

formation of green uranous salts, UX_4 , which act as powerful reducing agents.^{14a}

As the salts of uranic oxide are reduced in the absence of organic matter by the action of light, and as they impart a characteristic coloration to glass,¹⁵ they find a certain application to photography and glass work.^{15a}

the ground that with an atomic weight 120, uranium could not be placed in the periodic system. I think it will not be superfluous to add that—(1) in the other groups (K—Rb—Cs, Ca—Sr—Ba, Cl—Br—I) the acid character of the oxides decreases and their basic character increases with the rise of atomic weight, and therefore we should expect to find the same in the group Cr—Mo—W—U, and if CrO_3 , MoO_3 , WO_3 be the anhydrides of acids then we indeed find a decrease in their acid character, and therefore uranium trioxide, UO_3 , should be a very feeble anhydride, but its basic properties should also be very feeble. Uranic oxide does indeed show these properties, as was pointed out above (note 10). (2) Chromium and its analogues, beside the oxides RO_3 , also form lower grades of oxidation RO_2 , R_2O_3 , and the same is seen in uranium; it forms UO_3 , UO_2 , U_2O_3 and their compounds. (3) Molybdenum and tungsten, in being reduced from RO_3 , easily and frequently give an intermediate oxide of a blue colour, and uranium shows the same property, giving the so-called green oxide which, according to present views, must be regarded as $U_3O_8 = UO_2 \cdot 2UO_3$, analogous to Mo_3O_8 . (4) The higher chlorides, RCl_6 , possible for the elements of group VI. are either unstable (WCl_6) or do not exist at all (Cr); but there is one single lower volatile compound, which is decomposed by water, and is liable to further reduction into a non-volatile chlorine product and the metal. The same is observed in uranium, which forms an easily volatile chloride, UCl_4 , decomposed by water. (5) The high sp. gr. of uranium (18.6) is explained by its analogy to tungsten (sp. gr. 19.1). (6) For uranium, as for chromium and tungsten, yellow tints predominate in the form RO_3 , whilst the lower forms are green and blue. (7) Zimmermann (1881) determined the vapour densities of uranous bromide, UBr_4 , and chloride, UCl_4 , and they were found to correspond to the formulæ given above—that is, they confirmed the higher atomic weight, $U = 240$. Roscoe, a great authority on the metals of this group, was the first to accept the proposed atomic weight of uranium, $U = 240$, which since Zimmermann's work has been generally recognised.

^{14a} Uranium forms C_3U_2 in the electric furnace (1,000 ampères, 50 volts) with an excess of carbon. This carbide acts upon water with the formation of gaseous (CH_4 , C_2H_2 , &c.) and liquid hydrocarbons (Moissan, 1896).

¹⁵ Uranium glass, obtained by the addition of the yellow salt, $K_2U_2O_7$, to glass, has a greenish-yellow fluorescence, and is sometimes employed for ornaments; it absorbs the violet rays, like the other salts of uranic oxide—that is, it possesses an absorption spectrum in which the violet rays are absent. The index of refraction of the absorbed rays is altered, and they are given out again as greenish-yellow rays; hence compounds of uranic acid, when placed in the violet portion of the spectrum, emit a greenish-yellow light, and this forms one of the best examples (another is found in a solution of quinine sulphate) of the phenomenon of fluorescence. The rays of light which pass through uranic compounds do not contain the rays which excite the phenomena of fluorescence and of chemical transformation, as is proved by the researches of Stokes.

^{15a} Uranium stands out from all other known chemical elements in having the greatest atomic weight, and although belonging to the 12th series of group VI. (see Preface), in not having any known elements surrounding it in the periodic system. Thus neither VI. 11, VI. 13, V. 12, nor VII. 12 is known. Now, when the periodic law has been confirmed from the most varied aspects, it appears to me that there is much significance in these facts concerning uranium, more particularly since its connection with two of the most important—in many respects—discoveries in physics and chemistry made in our days, i.e., the discovery of the argon elements (especially of helium) and of the radioactive substances. Both present much that is unexpected and extreme in some yet

If we compare among the acid elements of group VI., sulphur, selenium, and tellurium, of the uneven series, with chromium,

deeply hidden way, connected with the extreme nature of the evolution of the elements of uranium itself. The greatest known concentration of mass of ponderable matter in the indivisible mass of the atom of uranium should already, *a priori*, produce peculiar qualities, although I am not in any way inclined (owing to the stern but fruitful discipline of inductive knowledge) to admit even the hypothetical transmutation of the elements into each other, and see no possibility of the argon or radio-active substances having originated from uranium or conversely. Being convinced that the investigation of uranium, starting from its native sources, will lead to many new discoveries, I am bold enough to recommend those who seek new subjects of research to occupy themselves with the uranium compounds, and may add that, for me personally, uranium has special interest owing to the prominent part it played in confirming the periodic law, inasmuch as its atomic weight, $U = 240$, was changed from $U = 120$ on the basis of this law, and was subsequently confirmed by experiment (Roscoe, Rammelsberg, Zimmermann, and others), which (together with the atomic weights of Ce and Be) convinced me of the universality of the law. Unfortunately the native minerals of uranium are not within the reach of many, owing to their extreme rarity.

Radio-active substances. In 1896 H. Becquerel discovered that uranium compounds have the faculty of emitting peculiar invisible rays (like the Röntgen and cathodic rays) which are given off constantly and independently without any visible expenditure of external energy (a marked difference from the Röntgen and cathodic rays). These rays are capable, (a) of producing, although somewhat slowly, chemical changes of various kinds, such as acting on a photographic plate and forming an image (which can be developed like an ordinary photograph), of tinting glass violet or brown (the coloration proceeds slowly but is permanent), of even ozonising air, &c.; (b) of penetrating through opaque bodies, for instance, through black paper, thin metallic discs, wood, &c. (this faculty for penetration is not quite alike for all radio-active rays, so that the latter cannot be considered as always uniform); (c) of causing such phosphorescent substances as zinc sulphide, barium platino-cyanide, &c., to become luminous in the dark (a considerable amount of radio-active matter is required to render this quite evident); (d) of rendering bodies subjected to these rays themselves temporarily (and sometimes for a considerable period) radio-active (this is a sort of induction, a temporary radio-activity. For instance, many of the objects in the laboratories, where much work has been done with these substances, acquire the same faculty, and the air no longer serves as an insulator); and (e) of communicating to the air, through which these rays pass, the faculty of rapidly causing electric discharges (in electroscopes*). The last property was chiefly investigated by Rutherford and Madame Curie, and gives the possibility of measuring the degree of radio-activity of substances, for, other conditions being similar (for instance, the pressure of the air), the faculty of discharging generally depends, not on the thickness of the layer of the radio-active substance, but only on its superficial area, the thickness of the layer of air, and the radio-activity of the substance under investigation, even in solution. In this respect it should be mentioned that the substances isolated by artificial means (as subsequently described) are hundreds of times more active than the native uranium minerals.

The unlooked-for peculiarity of the newly discovered properties incited many (and especially Professor and Madame Curie, Rutherford, Afanasieff, Giselle, and others) to follow Becquerel's example, and seek for radio-activity in different minerals and chemical reagents. It was at once found that this faculty belongs almost exclusively to the compounds of the two elements uranium and thorium, which are distinguished according to the periodic law by the fact that they possess the highest atomic weights of all the elements. It is particularly characteristic that the radio-activity is almost quite

* Phosphorus, in oxidising in damp air, also endows it with this property, or, as it is commonly said, ozonises the air. Le Bon (1900) observed that anhydrous sulphate of quinine, in absorbing moisture from the air, also ozonises it.

molybdenum, tungsten, and uranium, of the even series, we find that

independent of preliminary illumination, and in this respect is distinctly different from phosphorescence. Substances taken direct out of a mine or kept for a long time in darkness are just as radio-active as those which have been lying in the sunlight. A change of temperature also has little effect on the radio-activity. Metallic uranium fused in the electric furnace is as radio-active as that freshly prepared, but the activity apparently increases at the temperature of liquid air.

In general the radio-activity proved to be almost proportional to the amount of uranium or thorium present, so that the metal is more active than any of the compounds of uranium. But as some of the native uranium minerals, such as uranium copper ore, known as chalcocite, and some sorts of pitchblende, were found to be more radio-active than would follow from the proportion of uranium they contained, and even more active than the metal itself, and it was always possible to separate a more radio-active substance by fractionation, Professor and Madame Curie come to the conclusion that there must be a series of peculiar radio-active elements. So far three such elements are recognised: **radium**, which resembles barium; **polonium**, resembling bismuth; and **actinium**, resembling thorium (it separates out with iron); but of these, only radium has been obtained with any degree of purity. The compounds of radium, polonium, and actinium were extracted from the residues obtained in treating the uranium and thorium ores, but they are present in such small amounts that hardly more than a few decigrams of chloride of radium have yet been procured in a pure state from several tons of pitchblende. Uranium pitchblende has a very complex composition and contains a number of elements, in the separation of which, substances reacting like barium, bismuth, and thorium are also obtained, and it is these that contain the above radio-active elements. Thus, for example, polonium is separated together with bismuth, and if it is converted into sulphide of bismuth the first portions of the sublimate are found to be more radio-active and are regarded as a compound of polonium. Polonium is precipitated by H_2S from a very acid solution before bismuth, and is also precipitated from a nitric acid solution by water before the bismuth; antimony also deposits it from its solutions (Marckwald, 1902). Actinium was recognised by Debierne and separates out together with thorium, but it is precipitated before the latter by sodium hyposulphite and also by peroxide of hydrogen. **Radium** was obtained in the state of greatest purity by Professor and Madame Curie (in 1899-1902) by a process depending on the fact that chloride of radium is more soluble in water, alcohol, and hydrochloric acid than barium chloride. Carbonate of ammonium precipitates the radium carbonate only after the barium has been precipitated. Demarçay investigated the spectrum of radium and found it to resemble those of the metals of the alkaline earths; the most prominent lines (not proper to barium) given by the spark spectrum had wave-lengths of 482.6, 468.3, 453.3, 434.1, 381.5, and 365.0 millionths of a millimetre. Radium colours the flame carmine-red (Giselle). In 1902, Madame Curie found that the atomic weight of radium in its purest state was 223-225, or on the average about 224, if its chloride be given the composition RdCl_2 . This places it in group II., in the 12th series of the periodic system. The pure salt in a crystalline form is colourless and emits light in the dark; the crystals turn yellow or rose-colour after a time, but if redissolved again form colourless crystals. RdBr_2 , in ozonising the air, becomes alkaline, and Giselle (1902) then observed the formation of a highly radio-active gas which was not investigated. Further information respecting the chemical properties of the radio-active elements has not yet been obtained, and it should be mentioned that the existing data give some reason, if not for doubting the existence of the separate elements named above, at all events for not attributing radio-activity exclusively to them; that is, to regard it as a special state of matter rather than a property belonging exclusively to the atoms of certain elements, especially as this property at first appeared to belong to uranium* and thorium. More-

* Crookes considers that he obtained uranium quite free from radio-activity by subjecting the oxalate to fractional crystallisation.

the resemblance of the properties of the higher form, RO_3 , does not extend to the lower forms, and even entirely disappears in the elements, for there is not the smallest resemblance between sulphur and chromium and their analogues, in a free state. In other words, this means that the small periods, like Na, Mg, Al, Si, P, S, Cl, containing seven elements, do not contain any near analogues of chromium, molybdenum, &c., and therefore their true position among the other elements must be looked for only in those large periods which contain two small periods, and whose type is seen in the period containing: K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br. These large periods contain Ca and Zn, giving RO ; Sc and Ga of the third group, Ti and Ge giving RO_2 ; V and As forming R_2O_5 ; Cr and Se of the sixth group, Mn and Br of the seventh group, the remaining elements, Fe, Co, Ni, forming connective members of the intermediate eighth group, to the description of the representatives of which we shall turn in the following chapters. We shall now proceed to describe **manganese**, $\text{Mn}=55$, as an element of the seventh group of the even series, directly following after $\text{Cr}=52$, which corresponds with $\text{Br}=80$ to the same degree that Cr does with $\text{Se}=79$. For chromium, selenium, and bromine very close analogues are known, but for manganese as yet none have

over, Giselle showed that the radio-activity of preparations of radium increases with time, while in the case of polonium it decreases (like that of an induced body). Rutherford, by precipitating a solution of thorium with ammonia, almost to the end, obtained a residue which had a more intense activity, which it lost, however, in the course of time, although the precipitate of the chief mass of the hydrate of thorium was only slightly active at the beginning and gradually rose. Hofmann (1902) obtained preparations of uranium, &c., which had no radio-activity at all, but acquired it after being kept some time in a closed vessel. It is most remarkable that a copper or aluminum wire, electrified at the negative poles of a powerful Ruhmkorff's coil (having a potential of several thousand volts) becomes radio-active on its surface (Elster and Geitel, 1902), and that, if this superficial portion be removed, it gives a radio-active substance. In my opinion radio-activity must so far be regarded as a *property or state* into which many (but hardly all) substances may be brought, just as certain substances can be magnetised, and that radio-active substances may be looked upon as those which are able to pass into that state just as iron, steel, and cobalt can be magnetised. Moreover, it appears to me that radio-activity is probably connected with the power of a substance to absorb from, and emit into, the surrounding spaces some peculiar unknown substance, allied perhaps to that which forms ether of space and permeates all bodies. Two circumstances seem more especially to indicate that this is so: in the first place helium, argon, and the accompanying gases are found in a peculiar state (see Chap. V., p. 252) in the uranium and thorium minerals, and these gases apparently form a sort of transition to the substance which occupies space, as is seen from observations made on the solar corona, the aurora borealis, and similar phenomena; and in the second place Professor and Madame Curie and others, by heating native uranium compounds, obtained a gas which possessed radio-active properties, but not permanently. But in general this subject forms one of the most brilliant, and at the same time mysterious, discoveries of the close of the nineteenth century, and it is to be hoped that its elaboration (it is being studied by many men of science) will greatly help towards a true explanation of the existing data on light and electricity, and also ether.

been obtained—that is, it is the only representative of the even series in the seventh group. In placing manganese with the halogens in one group, the periodic system of the elements only requires that it should bear an analogy to the halogens in the higher type of oxidation—i.e., in the salts and acids—whilst it requires that as great a difference should be expected in the lower types and elements as there exists between chromium and sulphur or molybdenum and selenium. And this is actually the case. The elements of the seventh group form a higher salt-forming oxide, R_2O_7 , and its corresponding hydrate, HRO_4 , and salts—for example, $KClO_4$. Manganese in the form of potassium permanganate, $KMnO_4$, actually presents a great analogy in many respects to potassium perchlorate, $KClO_4$. The analogy of the crystalline form of both salts was shown by Mitscherlich. The salts of permanganic acid are also nearly all soluble in water, like those of perchloric acid, and if the silver salt of the latter, $AgClO_4$, is sparingly soluble in water, so also is silver permanganate, $AgMnO_4$. The specific volume of potassium perchlorate is equal to 55, because its specific gravity is 2.54; the specific volume of potassium permanganate is equal to 58, its specific gravity being 2.71. So that the volumes of equivalent quantities are in this instance approximately the same, whilst the atomic volumes of chlorine ($35.5/1.3=27$) and manganese ($55/7.5$) are in the ratio 4 : 1. In a free state the higher acids, $HClO_4$ and $HMnO_4$, are both soluble in water and volatile, both are powerful oxidisers—in a word, their analogy is still closer than that of chromic and sulphuric acids, and those points of distinction which they present also appear among the nearest analogues—for example, in sulphuric and telluric acids, in hydrochloric and hydriodic acids, &c. Besides Mn_2O_7 , manganese gives a lower degree of oxidation, MnO_3 , analogous to sulphuric and chromic trioxides, and with it corresponds potassium manganate, K_2MnO_4 , isomorphous with potassium sulphate.¹⁶ In the still lower grades of oxidation, Mn_2O_3 and MnO , there is hardly any similarity to chlorine, whilst every point of resemblance disappears when we come to the elements themselves—i.e., to manganese and chlorine—for manganese is a metal, like iron, which combines directly with chlorine to form a saline compound, $MnCl_2$, analogous to magnesium chloride.¹⁷

¹⁶ The comparison of potassium permanganate with potassium perchlorate, or of potassium manganate with potassium sulphate, shows directly that many of the physical and chemical properties of substances do not depend on the nature of the elements, but on the atomic types in which they appear, on the kind of movements, or on the positions in which the atoms forming the molecule occur.

¹⁷ If, however, we compare the spectra (Vol. I., p. 582) of chlorine, bromine, and iodine with that of manganese, a certain resemblance or analogy is to be found connecting manganese both with iron and with chlorine, bromine, and iodine.

Manganese belongs to the metals which are widely distributed in nature, especially in those localities where iron occurs, the ores of the latter frequently containing compounds of manganous oxide, MnO , which presents a resemblance to ferrous oxide, FeO , and to magnesia. In many minerals magnesia and the oxides allied to it are replaced by manganous oxide; calc spars and magnesites—i.e., $\text{R}''\text{CO}_3$ in general—are frequently met with containing manganous carbonate, which also occurs in a separate state, although but rarely. The soil also and the ash of plants generally contain a small quantity of manganese. In the analysis of minerals it is generally found that manganese occurs together with magnesia, because, like it, manganous oxide remains in solution in the presence of ammoniacal salts, not being precipitated by reagents. The property of this manganous oxide, MnO , of passing into the higher grades of oxidation under the influence of heat, alkalies, and air gives an easy means not only of discovering the presence of manganese in admixture with magnesia, but also of separating these two analogous bases. Magnesia is not able to give higher grades of oxidation, whilst manganese gives them with great facility. Thus, for instance, an *alkaline* solution of sodium hypochlorite produces a precipitate of manganese dioxide in a solution of a manganous salt: $\text{MnCl}_2 + \text{NaClO} + 2\text{NaHO} = \text{MnO}_2 + \text{H}_2\text{O} + 3\text{NaCl}$; whilst magnesia is not changed under these circumstances, and remains in the form of MgCl_2 . If the magnesia be precipitated owing to the presence of alkali, it may be dissolved in acetic acid, in which manganese dioxide is insoluble. The presence of small quantities of manganese may also be recognised by the green coloration which alkalies acquire when heated with manganese compounds in the air. This green coloration depends on the property of manganese of forming a still higher oxide and giving a green alkaline manganate corresponding to MnO_3 : $\text{MnCl}_2 + 4\text{KHO} + \text{O}_2 = \text{K}_2\text{MnO}_4 + 2\text{KCl} + 2\text{H}_2\text{O}$. Thus the faculty of oxidising in the presence of alkalies forms an essential character of manganese. The higher grades of oxidation containing Mn_2O_7 and MnO_3 are quite unknown in nature, and even MnO_2 is not so widely spread in nature as the ores composed of manganous compounds, which are met with nearly everywhere. The most important ore of manganese is its dioxide, or so-called **peroxide**, MnO_2 , which is known in mineralogy as **pyrolusite** (a black powder of sp. gr. 4.2). Manganese also occurs as an oxide corresponding with magnetic iron ore, $\text{MnO}, \text{Mn}_2\text{O}_3 = \text{Mn}_3\text{O}_4$, forming the mineral known as **hausmannite** (sp. gr. 4.3; brown powder). The oxide Mn_2O_3 also occurs in nature as the anhydrous mineral **braunite**, and in a hydrated form, $\text{Mn}_2\text{O}_3, \text{H}_2\text{O}$, called **manganite**. Both of these often occur as an admixture in pyrolusite. Besides

which, manganese is met with in nature as a rose-coloured mineral, **rhodonite**, or silicate, MnSiO_3 . Very fine and rich deposits of manganese ores have been found in the Caucasus, the Urals, and along the Dnieper. Those in the Sharapansky district of the government of Kutais and at Nicopol on the Dnieper are particularly rich. A large quantity of the ore (as much as 130,000 tons yearly) is exported from these localities.

Thus, manganese gives oxides of the following forms: MnO , manganous oxide, and manganous salts, MnX_2 , corresponding with the base, which resembles magnesia and ferrous oxide in many respects; Mn_2O_3 , a very feeble base, giving salts, MnX_3 , analogous to the aluminium and ferric salts, easily reduced to MnX_2 ; MnO_2 , dioxide, an almost indifferent or feebly acid oxide;¹⁸ MnO_3 , manganic anhydride, which forms salts resembling potassium sulphate;^{18a} Mn_2O_7 , permanganic anhydride, giving salts analogous to the perchlorates.

All the oxides of manganese when heated with acids give salts, MnX_2 , corresponding with the lower grade of oxidation, manganous oxide, MnO . Manganic oxide, Mn_2O_3 , is a feebly energetic base; it is true that it dissolves in hydrochloric acid and gives a dark solution containing the salt MnCl_3 , but the latter when heated evolves chlorine and gives a salt corresponding with manganous oxide, MnCl_2 —i.e., at first: $\text{Mn}_2\text{O}_3 + 6\text{HCl} = 3\text{H}_2\text{O} + \text{Mn}_2\text{Cl}_6$, and then the Mn_2Cl_6 decomposes into $2\text{MnCl}_2 + \text{Cl}_2$. None of the remaining higher grades of oxidation have a basic character, but **act as oxidising agents in the presence of acids**, disengaging oxygen and passing into salts, MnX_2 . Owing to this circumstance, **the manganous salts, MnX_2 , are often obtained**; they are, for instance, left in the residue when the dioxide is used for the preparation of oxygen and chlorine.¹⁹

¹⁸ Bisulphide of manganese, MnS_2 , corresponding to iron pyrites, FeS_2 , sometimes occurs in nature in fine octahedra (and cube combinations), for instance, in Sicily; it is called hauerite.

^{18a} On comparing the empirical composition of the manganates and the permanganates—for example, K_2MnO_4 with KMnO_4 —we find that they differ by one equivalent of the metal. Such a relation in composition produced by oxidation is of frequent occurrence—for instance, $\text{K}_4\text{Fe}(\text{CN})_6$ in oxidising gives $\text{K}_3\text{Fe}(\text{CN})_6$; H_2O forms HO or H_2O_2 , &c.

¹⁹ In the preparation of oxygen from the dioxide by means of H_2SO_4 , MnSO_4 is formed; in the preparation of chlorine from HCl and MnO_2 , MnCl_2 is obtained. It generally contains various impurities, and also a large amount of iron salts (from the native MnO_2), from which it cannot be freed by crystallisation. MnSO_4 is purified by mixing a portion of the liquid with a solution of sodium carbonate; a precipitate of manganous carbonate is then formed. This precipitate is collected and washed, and then added to the remaining mass of the impure solution of manganous sulphate; on heating the solution with this precipitate, the whole of the iron is precipitated as oxide. This is due to the fact that in the solution of the manganese dioxide in sulphuric acid the whole of the iron is converted into the ferric state (because the dioxide acts as an oxidising agent), which, as an exceedingly feeble base, precipitated by calcium carbonate and other kindred salts, separates out together with manganous carbonate. After being treated in this manner, the solution of manganous sulphate is easily purified by crystalli-

As the salts of manganous oxide closely resemble (and are isomorphous with) the salts of magnesia, MgX_2 , in many respects (with

sation. If it has a bright-red colour, this is due to the presence of higher grades of oxidation of manganese; they may be destroyed by boiling the solution, when the oxygen from the oxides of manganese is evolved and a very faintly coloured solution of manganous sulphate is obtained. This salt is remarkable for the facility with which it gives various combinations with water. By evaporating the almost colourless solution of **manganous sulphate** at very low temperatures, and by cooling the saturated solution at about 0° , crystals are obtained containing 7 atoms of water of crystallisation, $MnSO_4 \cdot 7H_2O$, which are isomorphous with cobaltous and ferrous sulphates. These crystals, even at 10° , lose 5 per cent. of water, and completely effloresce at 15° , losing about 20 per cent. of water. By evaporating a solution of the salt at the ordinary temperature, but not above 20° , crystals are obtained which contain 5 mols. of H_2O and are isomorphous with copper sulphate, whilst if the crystallisation is carried on between 20° and 30° , large transparent prismatic crystals are formed containing 4 mols. of H_2O (see Nickel). A boiling solution also deposits these crystals together with others containing $3H_2O$, whilst the first salt, when fused and boiled with alcohol, gives crystals containing 2 mols. of H_2O . Graham obtained a monohydrated salt by drying the salt at about 200° . The last atom of water is eliminated with difficulty, as is the case with all salts like $MgSO_4 \cdot nH_2O$. The crystals containing a considerable amount of water are rose-coloured, and the anhydrous crystals colourless. The solubility of $MnSO_4 \cdot 4H_2O$ (Chap. I., note 24) per 100 parts of water is: at 10° , 127 parts; at 37.5° , 149 parts; at 75° , 145 parts; and at 101° , 92 parts. Whence it is seen that at the boiling-point this salt is less soluble than at lower temperatures, and therefore a solution saturated at the ordinary temperature becomes turbid when boiled. Manganous sulphate, being analogous to magnesium sulphate, is decomposed, like the latter, when ignited; but it does not then leave manganous oxide, but the intermediate oxide, Mn_3O_4 . It gives double salts with the alkali sulphates. With aluminium sulphate it forms fine radiated crystals, whose composition resembles that of the alums—namely, $MnAl_2(SO_4)_4 \cdot 24H_2O$. This salt is readily soluble in water, and occurs in nature.

Manganous chloride, $MnCl_2$, crystallises with 4 mols. H_2O , like the ferrous salt, and not with 6 mols. like many kindred salts—for example, those of cobalt, calcium, and magnesium; 100 parts of water dissolve 38 parts of the anhydrous salt at 10° and 55 parts at 62° . Alcohol also dissolves manganous chloride, and the alcoholic solution burns with a red flame. This salt, like magnesium chloride, readily forms double salts. A solution of borax gives a dirty rose-coloured precipitate having the composition $MnH_4(BO_3)_2 \cdot H_2O$, which is used as a drier in paint-making. Potassium cyanide produces a yellowish-grey precipitate, MnC_2N_2 , with manganous salts, soluble in an excess of the reagent, a double salt, $K_4MnC_6N_6$, corresponding with potassium ferrocyanide being formed (Chap. XXII.). On evaporation of this solution, a portion of the manganese is oxidised and precipitated, whilst a salt corresponding to Gmelin's red salt, $K_3MnC_6N_6$ (see Chap. XXII.), remains in solution. Sulphuretted hydrogen does not precipitate salts of manganese, not even the acetate, but ammonium sulphide gives a flesh-coloured precipitate, MnS ; at 320° this sulphide of manganese passes into a green variety (Antony). Oxalic acid in strong solutions of manganous salts gives a white precipitate of the oxalate, MnC_2O_4 . This precipitate is insoluble in water, and is used for the preparation of manganous oxide itself, because it decomposes like oxalic acid when ignited (in a tube without excess of air), with the formation of carbonic anhydride, carbonic oxide, and manganous oxide. **Manganous oxide** thus obtained is a green powder, which, however, oxidises with such facility that it burns in air when brought into contact with an incandescent substance, and passes into the red intermediate oxide, Mn_3O_4 . In solutions of manganous salts, alkalis produce a precipitate of the hydroxide, MnH_2O_2 , which rapidly absorbs oxygen in the presence of air and gives the brown intermediate oxide (hydrate). Manganous oxide, besides being obtained by the above-described method from manganous oxalate, may likewise be obtained by igniting the higher oxides in a stream of

the exception of the fact that MnX_2 are rose-coloured and are easily oxidised in the presence of alkalis), we shall not dwell upon them, but limit ourselves to illustrating the chemical character of manganese by describing the metal and its corresponding acids. The single fact that the oxides of manganese are not reduced to the metal when ignited in hydrogen, and also from manganese carbonate. The manganous oxide ignited in the presence of hydrogen acquires a great density, and is no longer so easily oxidised. It may also be obtained in a crystalline form, if during the ignition of the carbonate or higher oxide a trace of dry hydrochloric acid gas be passed into the current of hydrogen. It is thus obtained in the form of transparent emerald-green crystals of the regular system, and in this state is easily soluble in acids.

Manganous oxide, in oxidising, gives the **red oxide of manganese**, Mn_2O_3 . This is the most stable of all the oxides of manganese; it is not only stable at the ordinary, but also at a high, temperature—that is, it does not absorb or disengage oxygen spontaneously. This oxide does not give any distinct salts, but it dissolves in sulphuric acid, forming a dark-red solution, which contains both manganous and manganic (of the **oxide**, Mn_2O_3) sulphates. The latter with potassium sulphate gives a manganese alum, in which the alumina is replaced by the isomorphous oxide of manganese. But this alum, like the solution of the intermediate oxide in sulphuric acid, evolves oxygen and leaves a manganous salt when slightly heated. Treated with nitric acid, Mn_2O_3 leaves MnO_2 (like red lead), and therefore Mn_2O_3 may be regarded as MnO, MnO_2 .

Manganese dioxide, MnO_2 , is still less basic than the oxide, and disengages oxygen or a halogen in the presence of acids, forming manganous salts, like the oxide. However, if it is suspended in ether, and hydrochloric acid gas passed into the mixture, which is kept cool, the ether acquires a green colour, owing to the formation of *tetrachloride of manganese*, $MnCl_4$ (corresponding with the dioxide), which passes into solution. It is, however, very unstable, being exceedingly easily decomposed, with the evolution of chlorine (Verron). The corresponding fluoride, MnF_4 , obtained by Nicklés is much more stable (because fluorine bears a greater resemblance to oxygen than chlorine). Nicklés obtained the fluoride by the action of RF on MnO_2 ; it forms double salts, like K_2MnF_6 . Manganese dioxide has rather an acid character, which is shown particularly in the compounds MnF_4 and $MnCl_4$ just mentioned, and in the property of manganese dioxide of combining with alkalis. If the higher grades of oxidation of manganese are deoxidised in the presence of alkalis, they usually give the dioxide combined with the alkali—for example, in the presence of potash a compound is formed which has the composition $K_2O, 5MnO_2$, showing the weak acid character of this oxide. When ignited in the presence of sodium compounds, manganese dioxide frequently forms $Na_2O, 8MnO_2$ and $Na_2O, 12MnO_2$, and lime when heated with MnO_2 gives from $CaO, 3MnO_2$ to $(CaO)_2, MnO_2$ (Rousseau) according to the temperature. Native psilomelane, Mn_3O_5 , may be regarded as $MnO, 2MnO_2$. Besides which MnO_2 is perhaps a saline compound, MnO, MnO_3 or $(MnO)_3, Mn_2O_7$, and there are reactions which support such a view (Spring, Richards, Traube, and others); for instance, it is known that manganous chloride and potassium permanganate give the dioxide in the presence of alkalis.

Manganese dioxide may be obtained from manganous salts by the action of oxidising agents. If manganous hydroxide or carbonate is shaken up in water through which chlorine is passed, the hypochlorite of the metal is not formed, as is the case with certain other oxides, but manganese dioxide is precipitated: $2MnO_2 \cdot H_2 + Cl_2 = MnCl_2 + MnO_2 \cdot H_2O + H_2O$. Owing to this fact, hypochlorites in the presence of alkalis and acetic acid, when added to a solution of manganous salts, give hydrated manganese dioxide, as was mentioned above. Manganous nitrate also leaves manganese dioxide when heated to 200° . It is also obtained from manganous and manganic salts of the alkalis, when they are decomposed in the presence of a small amount of acid: the practical method of converting the salts MnX_2 into the higher grades of oxidation is given in Chap. XI., note 6.

hydrogen (the oxides of iron give metallic iron under these circumstances), but only to manganous oxide, MnO , shows that manganese is difficult to reduce. A mixture of one of the oxides of manganese with charcoal or organic matter gives fused **metallic manganese** under the powerful heat developed by coke with an artificial draught. The metal was obtained for the first time in this manner by Gahn, after Pott, and more especially Scheele, had in the eighteenth century shown the difference between the compounds of iron and manganese (they were previously regarded as being the same). Manganese is prepared by the same methods as chromium (p. 314), but the purest product is obtained by decomposing Mn_3O_4 with aluminium powder or a strong solution of MnCl_2 with sodium amalgam. In the latter case, after the removal of mercury (at about 400°) a powder of manganese is obtained which fuses into a mass with difficulty owing to the ease with which it oxidises. In the first instance a fused metallic mass is obtained direct.²⁰ Its specific gravity varies between 7.3 and 8.0. It has a light-grey colour with a reddish tint, a feebly metallic lustre, and although it

²⁰ Former chemists often obtained manganese containing carbon. Moissan, by heating the oxides of manganese with carbon in the electric furnace, obtained carbide of manganese, Mn_3C , and remarked that the metal volatilised in the heat of the voltaic arc. Metallic manganese is not prepared on a large scale, nor its alloys with carbon (they readily and rapidly oxidise), but *ferro-manganese* or a coarsely crystalline alloy of iron, manganese, and carbon, which is smelted in blast-furnaces like pig-iron (see Chap. XXII.). This ferro-manganese is employed in the manufacture of steel by Bessemer's and other processes (see Chap. XXII.) and for the manufacture of manganese bronze. However, in America, Green and Wahl (1893) obtained almost pure metallic manganese on a large scale. They first treat the ore of MnO_2 with 30 per cent. sulphuric acid (which extracts all the oxides of iron present in the ore), and then heat it in a reducing flame to convert it into MnO , which they mix with a powder of Al (this is the prototype of Goldschmidt's method), lime and CaF_2 (as a flux), and heat the mixture in a crucible lined with magnesia; a reaction immediately takes place at a certain temperature, and a metal of specific gravity 7.3 is obtained, which contains only a small trace of iron.

Manganese gives two compounds **with nitrogen**, Mn_5N_2 and Mn_3N_2 . They were obtained by Prelinger (1894) from the amalgam of manganese, Mn_2Hg_3 (obtained on a mercury anode by the action of an electric current upon a solution of MnCl_2); the mercury may be removed from this amalgam by heating it in an atmosphere of hydrogen, and then metallic manganese is obtained as a grey porous mass of specific gravity 7.42. If this amalgam is heated in dry nitrogen, it gives Mn_5N_2 (grey powder, sp. gr. 6.58); but if heated in an atmosphere of NH_3 it gives (as also does Mn_5N_2) Mn_3N_2 (a dark mass with a metallic lustre, sp. gr. 6.21), which, when heated in nitrogen, is converted into Mn_5N_2 , and if heated in hydrogen, evolves NH_3 and disengages hydrogen from a solution of NH_4Cl . At all events, manganese is a metal which decomposes water and absorbs oxygen more easily than iron or cobalt. Among the alloys of manganese, besides those with iron, the copper alloys are most important. The alloy, containing 83 per cent. of Cu, 13 of Mn, and 4 of Ni, is called 'manganin' and is used for the wire of resistance batteries, because its electrical conductivity (after it has been repeatedly heated to 120°) varies very slightly within the usual range of temperature. The alloys with Cu, Sn, and Zn (bronzes) are very hard, and their properties can be easily modified at will, so that they are much used in practice.

is very hard, it can be scratched by a file. It rapidly oxidises in air, being converted into a black oxide; water acts on it with the evolution of hydrogen—this decomposition proceeds very rapidly with boiling water, or if the metal contains carbon.

It has been shown above that if manganese dioxide, or any lower oxide of manganese, is heated with an alkali in the presence of air, the mixture absorbs oxygen,²¹ and forms an alkaline manganate of a green colour: $2\text{KHO} + \text{MnO}_2 + \text{O} = \text{K}_2\text{MnO}_4 + \text{H}_2\text{O}$. Steam is disengaged during the ignition of the mixture, and if this does not take place, there is no absorption of oxygen. The oxidation proceeds much more rapidly if, before igniting in air, potassium chlorate or nitre is added to the mixture, and this is the method of preparing **potassium manganate**, K_2MnO_4 . With a small quantity of water the resultant mass gives a dark-green solution, which, when evaporated under the receiver of an air-pump over sulphuric acid, deposits green crystals of exactly the same form as potassium sulphate—namely, six-sided prisms and pyramids. The composition of the product is not changed by being redissolved, if perfectly pure water, free from air and carbonic acid, is taken. But in the presence of even very feeble acids, the solution of this salt changes its colour, becoming red and depositing manganese dioxide. The same decomposition takes place when the salt is heated with water, but when diluted with a large quantity of unboiled water manganese dioxide does not separate, although the solution turns red. This change of colour depends on the fact that potassium manganate, K_2MnO_4 , whose solution is green, is transformed into potassium permanganate, KMnO_4 , whose solution is of a red colour. The reaction proceeding under the influence of acids and a large quantity of water is expressed in the following manner: $3\text{K}_2\text{MnO}_4 + 2\text{H}_2\text{O} = 2\text{KMnO}_4 + \text{MnO}_2 + 4\text{KHO}$. If there is a large proportion of acid and the decomposition is aided by heat, the manganese dioxide and potassium permanganate are also decomposed, with formation of manganous salt. Exactly the same decomposition as takes place under the action of acids is also accomplished by magnesium sulphate, which reacts in many cases like an acid. When water containing atmospheric oxygen in solution acts on a solution of potassium manganate, the oxygen combines directly with the manganate and forms potassium permanganate, without precipitating manganese dioxide, $2\text{K}_2\text{MnO}_4 + \text{O} + \text{H}_2\text{O} = 2\text{KMnO}_4 + 2\text{KHO}$. (This reaction is not reversible; see note 22a.) Thus a solution of potassium manganate readily undergoes a very characteristic change in colour; hence this salt received the name of **mineral chameleon**.²²

²¹ Chap. III., note 7.

²² It was known to the alchemists by this name, but the true explanation of the

Potassium permanganate, KMnO_4 , crystallises in well-formed long red prisms with a bright-green metallic lustre. In the arts the potash is frequently replaced by soda and by other alkaline bases, but no salt of permanganic acid crystallises so well as the potassium salt, so that this salt is exclusively used in chemical laboratories. One part of the crystalline salt dissolves in 15 parts of water at the ordinary temperature. The solution is of a very deep **red colour**, which is so intense that it is still clearly observable after the liquid has been highly diluted with water. In a solid state it is decomposed by heat, with evolution of oxygen, a residue consisting of the lower oxides of manganese and potassium oxide being left.^{22a} A mixture of permanganate of potassium, phosphorus, and sulphur takes fire when struck or rubbed, but a mixture of the permanganate with carbon only takes fire when heated, not when struck. The instability of the salt is also seen from the fact that its solution is decomposed by peroxide of hydrogen, which at the same time it decomposes. A number of substances reduce potassium permanganate to manganese dioxide (in which case the red solution becomes colourless).²³ Many organic substances (although far from all, even when boiled in a solution of permanganate) act in this manner,

change in colour is due to the researches of Chevallot, Edwards, Mitscherlich, and Forehammer. The change in colour of potassium manganate is due to its instability and to its splitting up into two other manganese compounds, a higher and a lower: $3\text{MnO}_3 = \text{Mn}_2\text{O}_7 + \text{MnO}_2$. Manganese trioxide is really decomposed in this manner by the action of water (see later): $3\text{MnO}_3 + \text{H}_2\text{O} = 2\text{MnHO}_4 + \text{MnO}_2$ (Franke, Thorpe, and Humbly). The instability of the salt is proved by the fact of its being deoxidised by organic matter, with the formation of manganese dioxide and alkali, so that a solution of this salt cannot, for instance, be filtered through paper. The presence of an excess of alkali increases the stability of the salt; when heated, it breaks up in the presence of water, with the evolution of oxygen.

The method of preparing **potassium permanganate** will be understood from the above. There are many recipes for preparing this substance, as it and the sodium salt as well are now used in considerable quantities for technical and laboratory purposes. But in all cases the essence of the methods is one and the same. This solution may be boiled, as the liquid will contain free alkali; but the solution cannot be evaporated to dryness, because a strong solution, as well as the solid salt, is decomposed by heat.

By adding a dilute solution of manganous sulphate to a boiling mixture of lead dioxide and dilute nitric acid, the whole of the manganese may be converted into permanganic acid (Crum).

^{22a} The solution of this salt with an excess of impure commercial alkali generally acquires a green tint, owing to the formation of a manganous salt, a portion of the oxygen being transferred to the organic matter present in the alkali. Pure solutions of alkalis do not produce this coloration, even after boiling and evaporation.

²³ A solution of potassium permanganate gives a beautiful absorption spectrum (Chap. XIII.). We may here remark that a dilute solution of permanganate of potassium forms a colourless solution with nickel salts, because the green colour of the solutions of nickel salts is complementary to the red. Such a decolorised solution, containing a large proportion of nickel and a small proportion of manganese, decomposes after a time, throws down a precipitate, and re-acquires the green colour proper to the nickel salts.

being oxidised at the expense of a portion of their oxygen. Thus, a solution of sugar decomposes a cold solution of potassium permanganate. In the presence of an excess of alkali, with a small quantity of sugar, the reduction leads to the formation of potassium manganate, $2\text{KMnO}_4 + 2\text{KHO} = \text{O} + 2\text{K}_2\text{MnO}_4 + \text{H}_2\text{O}$. With a considerable amount of sugar and a more prolonged action, the solution turns brown and precipitates manganese dioxide or even the oxide. In the oxidation of organic bodies by an alkaline solution of KMnO_4 , three-eighths of the oxygen in the salt are generally utilised for oxidation: $2\text{KMnO}_4 = \text{K}_2\text{O} + 2\text{MnO}_2 + \text{O}_3$. A portion of the alkali liberated is retained by the manganese dioxide, and the other portion generally combines with the substance oxidised, because the latter most frequently gives an acid with an excess of alkali. A solution of potassium iodide acts in a similar manner, being converted into potassium iodate at the expense of the three atoms of oxygen disengaged by two molecules of potassium permanganate.

In the presence of acids, potassium permanganate acts as an oxidising agent with still greater energy than in the presence of alkalies. At any rate, a greater proportion of oxygen is then available for oxidation, namely, not $\frac{3}{8}$, as in the presence of alkalies, but $\frac{5}{8}$, because in the first instance manganese dioxide is formed, and in the second case manganous oxide, or rather the salt, MnX_2 , corresponding with it. Thus, for instance, in the presence of an excess of sulphuric acid, the decomposition is accomplished in the following manner: $2\text{KMnO}_4 + 3\text{H}_2\text{SO}_4 = \text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 3\text{H}_2\text{O} + 5\text{O}$. This decomposition, however, does not proceed directly on mixing a solution of the salt with sulphuric acid, and crystals of the salt even dissolve in oil of vitriol without the evolution of oxygen, and this solution only decomposes by degrees after a certain time. This is due to the fact that sulphuric acid liberates free permanganic acid from the permanganate,²¹ which acid is stable

²¹ If sulphuric acid is allowed to act on potassium permanganate without any special precautions, a large amount of oxygen is evolved (it may even explode and inflame), and a violet spray of the decomposing permanganic acid is given off. But if the pure salt (i.e., free from chlorine) is dissolved in pure well-cooled sulphuric acid, without any rise in temperature, a green-coloured liquid settles at the bottom of the vessel. This liquid does not contain any sulphuric acid, and consists of permanganic anhydride, Mn_2O_7 (Asehoff, Terrell). It is impossible to prepare any considerable quantity of the anhydride by this method, as it decomposes with explosion as it accumulates, evolving oxygen. Mn_2O_7 , in dissolving in sulphuric acid, gives a green solution, which (according to Franke, 1887) contains a compound $\text{Mn}_2\text{SO}_{10} = (\text{MnO}_3)_2\text{SO}_4$ —that is, sulphuric acid in which both hydrogens are replaced by the group MnO_3 , which is combined with OK in permanganate of potassium. This compound with a small quantity of water gives Mn_2O_7 ; with NaCl in the cold it gives MnO_3Cl (i.e., the chloranhydride of manganic acid), which liquefies in the cold and is very unstable; and when heated to 30° , it gives manganous anhydride or manganese trioxide, $(\text{MnO}_3)_2\text{SO}_4 + \text{H}_2\text{O} = 2\text{MnO}_3 + \text{H}_2\text{SO}_4 + \text{O}$. Pure

in solution. But if, in the presence of acids and a permanganate, there is a substance capable of absorbing oxygen—capable, for instance, of passing into a state of higher oxidation—then the reduction of the permanganic acid into manganous oxides sometimes proceeds directly at the ordinary temperature. This reduction is very clearly seen, because the solutions of potassium permanganate are red, whilst the manganous salts are almost colourless. Thus, for instance, nitrous acid and its salts are converted into nitric acid and decolorise the acid solution of the permanganate. Sulphurous anhydride and its salts immediately decolorise potassium permanganate, forming sulphuric acid. Ferrous salts, and, in general, salts of lower grades of oxidation capable of being oxidised in solution, act in exactly the same manner. Sulphuretted hydrogen is also oxidised to sulphuric acid; even mercury is oxidised at the expense of permanganic acid, and decolorises its solution, being converted into mercuric oxide. Moreover, the end point of these reactions may be easily seen, and therefore, having first determined the amount of active oxygen in one volume of a solution of potassium permanganate, and knowing how many volumes are required to effect a given oxidation, it is easy to determine the amount of an oxidisable substance in a

manganese trioxide is obtained if the solution of $(\text{MnO}_3)_2\text{SO}_4$ is poured in drops on to sodium carbonate. Then, together with carbonic anhydride, a spray of manganese trioxide passes over, which may be collected in a well-cooled receiver, and this shows that the reaction proceeds according to the equation: $(\text{MnO}_3)_2\text{SO}_4 + \text{Na}_2\text{CO}_3 = \text{Na}_2\text{SO}_4 + 2\text{MnO}_3 + \text{CO}_2 + \text{O}$ (Thorpe). The trioxide is decomposed by water, forming manganese dioxide and a solution of **permanganic acid**: $3\text{MnO}_3 + \text{H}_2\text{O} = \text{MnO}_2 + 2\text{HMnO}_4$. The same acid is obtained by dissolving permanganic anhydride in water.

Barium permanganate, $\text{Ba}(\text{MnO}_4)_2$, when treated with sulphuric acid gives a red solution of the same acid. This barium salt may be prepared by the action of barium chloride on the difficultly soluble silver permanganate, AgMnO_4 , which is precipitated on mixing a strong solution of the potassium salt with silver nitrate. A solution of permanganic acid deposits manganese dioxide when exposed to the action of light, and also when heated above 60° , and this proceeds the more rapidly the more dilute the solution. Even hydrogen gas is absorbed by a solution of permanganic acid; and charcoal and sulphur are also oxidised by it, as they are by potassium permanganate. Finely divided platinum immediately decomposes permanganic acid. With potassium iodide it liberates iodine (which may afterwards be oxidised into iodic acid). Ammonia is oxidised with evolution of nitrogen. The oxidising action of permanganic acid in a strong solution may be accompanied by flame and the formation of violet fumes of permanganic acid; thus a strong solution of it takes fire when brought into contact with paper, alcohol, alkaline sulphides, fats, &c.

We may add that, according to Franke, 1 part of potassium permanganate with 13 parts of sulphuric acid at 100° gives brown crystals of the salt $\text{Mn}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$, which yields a precipitate of hydrated manganese dioxide, $\text{H}_2\text{MnO}_3 = \text{MnO}_2 \cdot \text{H}_2\text{O}$, when treated with water.

Spring, by precipitating potassium permanganate with sodium sulphite and washing the precipitate by decantation, obtained a soluble colloidal manganous oxide, whose composition was intermediate between Mn_2O_3 and MnO_2 —namely, $\text{Mn}_2\text{O}_3 \cdot 4(\text{MnO}_2 \cdot \text{H}_2\text{O})$. MnO and Mn_2O_7 apparently volatilise without decomposition under a low pressure.

solution from the amount of permanganate expended (Marguerite's method).

The oxidising action of KMnO_4 , like all other chemical reactions, is not accomplished instantaneously, but only gradually. And, as the course of the reaction is here easily followed by determining the amount of salt unchanged in a sample taken at a given moment,²⁵ the oxidising reaction of potassium permanganate, in an acid liquid, was employed by Harcourt and Esson (1865) as one of the first cases for the investigation of the laws of the **rate of chemical change**,²⁶ a subject of great importance in chemical mechanics. In their experiments they took oxalic acid, $\text{C}_2\text{H}_2\text{O}_4$, which in oxidising gives carbonic anhydride, whilst, with an excess of sulphuric acid, the potassium permanganate is converted into manganous sulphate, MnSO_4 , so that the ultimate oxidation will be expressed by the equation: $5\text{C}_2\text{H}_2\text{O}_4 + 2\text{MnKO}_4 + 3\text{H}_2\text{SO}_4 = 10\text{CO}_2 + \text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 8\text{H}_2\text{O}$. The influence of the relative amount of sulphuric acid is seen from the annexed table, which gives

²⁵ For rapid and accurate determinations of this kind, advantage is taken of those methods of chemical analysis which are known as 'titrations,' and consist in measuring the volume of solutions of known strength required. Details respecting the theory and practice of titration, in which potassium permanganate is very frequently employed, must be looked for in works on analytical chemistry.

²⁶ The measurements of velocity and acceleration serve for determining the measure of forces in mechanics, but in that case the velocities are magnitudes of length or paths passed over in a unit of time. The velocity of chemical change embodies a conception of quite another kind. In the first place, the velocities of reactions are magnitudes of the masses which have entered into chemical transformations; in the second place, these velocities can only be relative quantities. Hence the conception of 'velocity' has quite a different meaning in chemistry from that it has in mechanics. Their only common factor is time. If Δt be the increment of time and Δx the quantity of a substance changed in this space of time, then the fraction (or quotient) $\Delta x/\Delta t$ will express the rate of the reaction. The natural conclusion, arrived at both by Harcourt and Esson, and previously to them (1850) by Wilhelmj (who investigated the rate of conversion, or inversion, of sugar in its passage into dextrose and levulose), is that this velocity is proportional to the quantity of substance still unchanged—i.e., that $\Delta x/\Delta t = C(A-x)$, where C is a constant coefficient of proportionality, and A is the quantity of a substance taken for reaction at the moment when $t=0$ and $x=0$ —that is, at the beginning of the experiment, from which the time t and quantity x of substance changed are counted. On integrating the preceding equation, we obtain $\log [A/(A-x)] = kt$, where k is a constant. Hence, knowing A , x , and t , for each reaction, we find k , and it proves to be a constant quantity. Thus, from the figures cited in the text for the reaction: $2\text{KMnO}_4 + 10\text{C}_2\text{H}_2\text{O}_4 + 14\text{MnSO}_4$, it may be calculated that $k=0.0114$; for example, $t=44$, $x=68.4$ ($A=100$), whence $kt=0.5004$ and $k=0.0114$ (see also Chap. XIX., note 3, and Chap. XXII., note 25a).

The researches made by Hood, van't Hoff, Ostwald, Warder, Menschutkin, Konovoloff, and others have a particular significance in this direction. I consider it impossible to enter into the details of this province of theoretical chemistry, although I am quite confident that its development should lead to very important results, especially in respect to chemical equilibria, for van't Hoff has already shown that the limit of reaction in reversible reactions is determined by the attainment of equal velocities for the opposite reactions.

the measure of reaction, p , per 100 parts of potassium permanganate, taken four minutes after mixing, using n molecules of sulphuric acid, H_2SO_4 , per $2\text{KMnO}_4 + 5\text{C}_2\text{H}_2\text{O}_4$:

$n = 2$	4	6	8	12	16	22
$p = 22$	36	51	63	77	86	92

showing that in a given time (4 minutes) the oxidation is the more perfect the greater the amount of sulphuric acid taken for given amounts of KMnO_4 and $\text{C}_2\text{H}_2\text{O}_4$. It is obvious also that the temperature and relative amount of every one of the acting and resulting substances should show their influence on the relative velocity of reaction : thus, for instance, direct experiment showed the influence of the admixture of manganous sulphate. When a large proportion of oxalic acid (108 molecules) was taken to a large mass of water and to 2 molecules of permanganate 14 molecules of manganous sulphate were added, the quantity, x , of the potassium permanganate acted on (in percentages of the potassium permanganate taken) in t minutes (at 16°) was as follows :

$t=2$	5	8	11	14	44	47	53	61	68
$x=5.2$	12.1	18.7	25.1	31.3	68.4	71.7	75.8	79.8	83.0

The same phenomena are observed in every case which has been investigated, and this branch of theoretical or physical chemistry, now studied by many, promises to explain the course of chemical transformations from a fresh point of view, which is closely allied to the doctrine of affinity, because the rate of reaction is without doubt connected with the magnitude of the affinities acting between the reacting substances.

CHAPTER XXII

IRON, COBALT, AND NICKEL

JUDGING from the atomic weights, and the forms of the higher oxides of the elements already considered, it is easy to form an idea of the seven groups of the periodic system. Such are, for instance, the typical series Li, Be, B, C, N, O, F, or the third series, Na, Mg, Al, Si, P, S, Cl. The seven usual types of higher oxides from R_2O to R_2O_7 correspond with them (Chap. XV.). The position of the eighth group is quite separate, and is determined by the fact that, as we have already seen, in each group of metals having a greater atomic weight than potassium, a distinction ought to be made between the elements of the even and those of the uneven series. The series of even elements, commencing with a strikingly alkaline element (potassium, rubidium, caesium), together with the uneven series following it, and concluding with a haloid (bromine, iodine), forms a large period, the properties of whose members repeat themselves in other similar periods. The elements of the eighth group are situated between the elements of the even series and the elements of the uneven series following them in these larger periods (see Preface). The properties of the elements belonging to group VIII., in many respects independent and striking, are shown with typical clearness in the case of iron, which resembles manganese in many respects, and is the well-known representative of this group.

Iron is one of those elements which are widely diffused, not only in the crust of the earth, but also throughout the entire universe. Its oxides and other compounds are found in the most diverse portions of the earth's crust; but iron is not found on the earth's surface in a free state, because it easily oxidises under the action of air. It is occasionally found in the native state in meteorites, or aërolites, which fall upon the earth.

Meteoric iron is formed outside the earth.¹ Meteorites are fragments which are carried round the sun in orbits, and fall upon the earth

¹ The composition of meteoric iron is variable. It generally contains nickel, phosphorus, carbon, &c. The schreibersite of meteoric stones contains Fe_3Ni_2P .

when coming into proximity with it during their motion in space. The meteoric dust, on passing through the upper parts of the atmosphere, and becoming incandescent from friction with the gases, produces that phenomenon which is familiar under the name of 'falling stars.'² Such

² Comets and the rings of Saturn ought now to be considered as consisting of an accumulation of such meteoric cosmic solid particles or bodies. Perhaps the part played by these minute bodies scattered throughout space is much more important in the formation of the largest celestial bodies than has hitherto been imagined. The investigation of this branch of astronomy, due to Schiaparelli, and begun in the last decades of the nineteenth century, has a bearing on the whole of natural science.

The question arises as to why the iron in meteorites is in a free state, whilst on the earth it is in a state of combination. Does not this tend to show that the condition of our globe is very different from that of the rest? My answer to this question has been already given in Vol. I., Chap. VIII., note 57. It is my opinion that inside the earth there is a mass similar in composition to meteorites—that is, containing rocky matter and metallic iron, partly carburetted. In conclusion, I consider it will not be out of place to add the following explanations. According to the theory of the distribution of pressures (see my treatise *On Barometric Levelling*, 1876, p. 48 *et seq.*) in an atmosphere of mixed gases, it follows that two gases, whose densities are d and d_1 , and whose relative quantities or partial pressures at a certain distance from the centre of gravity are h and h_1 , will, when at a greater distance from the centre of attraction, present a different ratio of their masses $x : x_1$ —that is, of their partial pressures—which may be found by the equation $d_1(\log h - \log x) = d(\log h_1 - \log x_1)$. If, for instance, $d : d_1 = 2 : 1$, and $h = h_1$ (that is to say, the masses are equal at the lower height) = 1000, then when $x = 10$ the magnitude of x_1 will not be 10 (i.e., the mass of a gas at a higher level whose density is 1 will not be equal to the mass of a gas whose density is 2, as was the case at a lower level), but much greater—namely, $x_1 = 100$ —that is, the lighter gas will predominate over a heavier one at a higher level. Therefore, when the whole mass of the earth was in a state of vapour, the substances having a greater vapour density (speaking relatively, for instance, to a unit of mass of oxygen) accumulated about the centre and those with a lesser vapour density at the surface. And as the vapour densities depend on the atomic and molecular weights, those substances which have small atomic and molecular weights ought to have accumulated at the surface, and those with high atomic and molecular weights, which are the least volatile and the easiest to condense, at the centre. Thus it becomes apparent why such light elements as hydrogen, carbon, nitrogen, oxygen, sodium, magnesium, aluminium, silicon, phosphorus, sulphur, chlorine, potassium, calcium, and their compounds predominate at the surface and largely form the earth's crust. There is also now much iron in the sun, as spectrum analysis shows, and therefore it must have entered into the composition of the earth and other planets, but would have accumulated at the centre, because the density of its vapour is certainly large and it easily condenses. There was also oxygen near the centre of the earth, but not sufficient to combine with the iron. The former, as a much lighter element, accumulated principally at the surface, where we at the present time find all oxidised compounds and even a remnant of free oxygen. This gives the possibility not only of explaining, in accordance with cosmogonic theories, the predominance of oxygen compounds on the surface of the earth, with the occurrence of unoxidised iron in the interior of the earth and in meteorites, but also of understanding why the density of the whole earth (over 5) is far greater than that of the rocks (1 to 3) composing its crust. And if all the preceding arguments and theories be true, it must be admitted that the interior of the earth and other planets contains metallic (unoxidised) iron, which, however, is only found on the surface as aërolites. And then, assuming that aërolites are the fragments of planets which have crumbled to pieces, as it were, during cooling (this has been held to be the case by astronomers, judging from the paths of aërolites), it is readily understood why they should be composed of metallic iron, and this would explain its occurrence in

is the doctrine concerning meteorites, and the fact of their containing rocky (silicious) matter and metallic iron shows, therefore, that outside the earth the elements and their aggregation are in some degree the same as upon the earth itself.

The most widely diffused terrestrial compound of iron is iron bisulphide, FeS_2 , or **iron pyrites**. It occurs in formations of both aqueous and igneous origin, and sometimes in enormous masses. It is a substance having a greyish-yellow colour, with a metallic lustre, and a specific gravity of 5.0; it crystallises in the regular system.^{2a}

The oxides are the principal ores used for producing metallic iron. The majority of the ores contain ferric oxide, Fe_2O_3 , either in a free state or combined with water, or else in combination with ferrous oxide, FeO . **Ferric oxide** in a separate form appears sometimes as crystals of the rhombohedral system, having a metallic lustre and greyish steel colour; they are brittle, and form a red powder, and have a specific gravity of about 5.25. In type of oxidation and properties ferric oxide resembles alumina; it is, however, although with difficulty, soluble in acids, even when anhydrous. The crystalline oxide bears the name of **specular iron ore**, but ferric oxide most often occurs in a non-crystalline form in masses having a red fracture, and is then known as **red hæmatite**. In this form, however, it is rather a rare ore, and is principally found in veins. The hydrates of ferric oxide, **ferric hydroxides**,³ are most often found in aqueous or stratified formations,

the depths of the earth, which we assumed as the basis of our theory of the formation of naphtha (Chap. VIII., notes 57–60). Grains of metallic iron have been found disseminated in certain basalts or volcanic rocks on the surface of the earth, and may have proceeded from iron in the interior of the earth.

^{2a} Immense deposits of iron pyrites are known in various parts of Russia. On the river Msta, near Borovitsi, thousands of tons are yearly collected from the detritus of the neighbouring rocks. In the governments of Toula, Riazan, and in the Donetz district, continuous layers of pyrites occur among the coal seams. Very thick beds of pyrites are also known in many parts of the Caucasus. But the deposits of the Urals are particularly vast, and have been worked for a long time. Amongst these I shall indicate only the deposits on the Soymensky estate, near the Kishteimsky Works; the Kaletinsky deposits, near the Virhny-Isetsy Works (containing 1–2 per cent. Cu); on the banks of the river Koushaivi, near Koushvi (3–5 per cent. Cu); and the deposits near the Bogoslovsky Works (3–5 per cent. Cu). Iron pyrites (especially that containing copper which is extracted after roasting) is now chiefly employed for roasting, as a source of SO_2 for the manufacture of sulphuric acid; but the remaining oxide of iron is perfectly suitable for smelting into pig iron, although it gives a sulphurous pig iron (the sulphur may be easily removed by subsequent treatment, especially with the aid of ferro-manganese in Bessemer's process). The great technical importance of iron pyrites leads to its sometimes being imported from great distances; for instance, into England from Spain. Besides which, when heated in closed retorts, FeS_2 gives sulphur, and, if allowed to oxidise in damp air, green vitriol, FeSO_4 .

³ The hydrated ferric oxide is found in nature in a dual form. It is somewhat rarely met with in the form of a crystalline mineral called **gothite**, whose specific gravity is 4.4 and composition $\text{Fe}_2\text{H}_2\text{O}_4$, or FeHO_2 , or $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$; it is most frequently found

and are known as **brown hæmatites**; they generally have a brown colour, form a yellowish-brown powder, and have no metallic lustre, but an earthy appearance. They dissolve easily in acids and diffuse through other formations, especially clays (for instance, ochre); they sometimes occur in reniform and similar masses, evidently of aqueous origin. Such are, for instance, the so-called *bog* or *lake* and *peat* ores found at the bottom of marshes and lakes, and also under and in peat beds. This ore is formed from water containing ferrous carbonate in solution, which, after absorbing oxygen, deposits ferric hydroxide. In rivers and springs, iron is found as ferrous carbonate, held in solution, like CaCO_3 , through the agency of carbonic acid; hence the existence of chalybeate springs containing FeCO_3 . This ferrous carbonate, or **siderite**, is either found as a non-crystalline product of evidently aqueous origin, or as a crystalline spar called **spathic iron ore**. The reniform deposits of the former are most remarkable; they are called **sphaerosiderites**, and sometimes form whole strata in the Jurassic and Carboniferous formations. **Magnetic iron ore**, $\text{Fe}_3\text{O}_4 = \text{FeO}, \text{Fe}_2\text{O}_3$, in virtue of its purity and practical uses, is a very important ore; it is a compound of ferrous and ferric oxides, is naturally magnetic, has a specific gravity of 5.1, crystallises in well-formed crystals of the regular system, is with difficulty soluble in acids, and sometimes forms enormous masses, as, for instance, Mount Blagodatskiy in the Central Urals, and Mount Magnitni in the Southern Urals. However, in most cases—for instance, at Korsak-Mogila (to the north of Berdiansk and Nogaiska, near the Sea of Azov), or at Krivoi Rog (to the west of Ekaterinoslav)—the magnetic iron ore is mixed with other iron ores. In the Urals, the Caucasus (without mentioning Siberia), and in the district adjoining the basin of the Don, Russia possesses the richest iron ores in the world. To the south of Moscow, in the governments of Toula and Nijni-novgorod, in the Olonetz district, and in the government of Orloffsky (near Zinovieff in the district of Kromsky), and in many other places, there are likewise abundant supplies of iron ores amongst the deposited aqueous formations; the siderite of Orloffsky, for instance, is distinguished by its great purity.⁴

as brown ironstone, forming a dense mass of fibrous reniform deposits of the composition $2\text{Fe}_2\text{O}_3, 3\text{H}_2\text{O}$. In bog ore and other similar ores we most often find a mixture of this hydrated ferric oxide with clay and other impurities.

⁴ The ores of iron, like many other minerals, are worked by means of vertical, horizontal, or inclined shafts which reach and penetrate the veins and strata containing the ore deposits. The mass of ore excavated is raised to the surface, then sorted, and subjected to roasting and other treatment. In every case the ore contains foreign matter. In the extraction of iron, which is the cheapest metal, the dressing of an ore is in most cases unprofitable, and only ores rich in metal are worked—namely, those containing at least 20 per cent. It is often profitable to transport very rich and pure ores

Iron is also found in the form of various other compounds—for instance, in certain silicates, and also in some phosphates—but these forms are comparatively rare in nature in a pure state, and have not the industrial importance of those natural compounds of iron previously mentioned. In small quantities iron enters into the composition of every kind of soil and of all rocky formations. As ferrous oxide, FeO , is isomorphous with magnesia, and ferric oxide, Fe_2O_3 , with alumina, isomorphous substitution is here possible, and hence minerals are not infrequently found in which the quantity of iron varies considerably; such, for instance, are pyroxene, amphibole, certain varieties of mica, &c. Although much iron oxide is deleterious to the growth of vegetation, still plants do not flourish without iron; it enters as an indispensable component into the composition of all organisms; in the ash of plants we always find more or less of its compounds. It also occurs in blood, and forms one of the colouring matters in it; 100 parts of the blood of the highest organisms contain about 0.05 of iron.

The reduction of the ores of iron into metallic iron is in principle very simple, because when the oxides of iron are strongly heated with charcoal, hydrogen, carbonic oxide, and other reducing agents,⁵

(with as much as 70 per cent. of iron) from long distances. The details concerning the working and extraction of metals will be found in special treatises on metallurgy and mining.

⁵ The reduction of iron oxides by hydrogen belongs to the order of reversible reactions, and is therefore determined by a limit which is here expressed by the attainment of the same pressure as in the case where hydrogen acts on iron oxides, and as in the case where (at the same temperature) water is decomposed by metallic iron. The calculations referring to this matter were made by Henri Sainte-Claire Deville (1870). Spongy iron was placed in a tube having a temperature t , one end of which was connected with a vessel containing water at 0° (vapour pressure = 4.6 mm.) and the other end with a mercury pump and pressure gauge which determined the limiting pressure, p , attained by the dry hydrogen (subtracting the pressure of the water vapour from the pressure observed). A tube was then taken containing an excess of iron oxide. It was filled with hydrogen, and the pressure p_1 of the residual hydrogen observed when the water was condensed at 0° .

$t = 200^\circ$	440°	860°	1040°
$p = 95.9$	25.8	12.8	9.2 mm.
$p_1 = \text{—}$	—	12.8	9.4 mm.

The equality of the pressure of the hydrogen in the two cases is evident.

By taking ferric oxide, Fe_2O_3 , Moissan observed that at 350° it passed into magnetic oxide, Fe_3O_4 ; at 500° , into ferrous oxide, FeO ; and at 600° , into metallic iron. Wright and Luff (1878) found that (a) the temperature of reaction depends on the condition of the oxide taken; for instance, precipitated ferric oxide is reduced by hydrogen at 85° , that obtained by oxidising the metal or from its nitrate at 175° ; (b) when other conditions are the same, the reduction by carbonic oxide commences earlier than that by hydrogen, and the reduction by hydrogen still earlier than that by charcoal; (c) the reduction is effected with greater facility when a greater quantity of heat is evolved during the reaction. Ferric oxide obtained by heating ferrous sulphate to a red heat begins to be reduced by carbonic oxide at 202° , by hydrogen at 260° , by charcoal at 430° , whilst for magnetic oxide, Fe_3O_4 , the temperatures are 200° , 290° , and 450° respectively.

they easily give metallic iron. But the matter is rendered more difficult by the fact that the iron does not melt at the heat developed by the combustion of the charcoal, and therefore it does not separate from those mechanically mixed impurities which are found in the iron ore. This is obviated by the following very remarkable property of iron: at a high temperature it is capable of combining with a small quantity (from 2 to 5 per cent.) of carbon, and then forms **cast iron**, which easily **melts** in the heat developed by the combustion of charcoal in air. For this reason metallic iron is not obtained directly from the ore, but is only formed after the further treatment of the cast iron, the first product extracted from the ore being cast iron containing carbide of iron.^{5a} The fused mass of cast iron disposes itself in the furnace below the slag—that is, the impurities of the ore fused by the heat of the furnace. If these impurities did not fuse they would block up the furnace in which the ore was being smelted, and the continuous smelting of the cast iron would not be possible;⁶ it would be necessary periodically to cool the furnace and heat it up again, which means a wasteful expenditure of fuel, and hence in the production of cast iron the object in view is to obtain all the earthy impurities of the ore in the shape of a fused mass or slag. Only in rare cases does the ore itself form a mass which fuses at the temperature employed, and these cases are objectionable if much iron oxide is carried away in the slag. The impurities of the ores most often consist of certain mixtures—for instance, a mixture of clay and sand, or a mixture of limestone and clay, or quartz, &c. These impurities do not separate of themselves, or do not fuse. The difficulty of the industry lies in forming an easily fusible slag, into which the whole of the foreign matter of the ore would pass and flow down to the

^{5a} With iron, carbon most easily and frequently forms a carbide having the composition Fe_3C (6·7 per cent. of C). Abel first extracted it from steel, and Moissan showed that it is formed directly in the electric furnace by saturating iron with carbon. When this alloy, or cast iron saturated with carbon, is formed and the heating of the mass prolonged, a moment occurs when it becomes so viscid that it cannot be poured from the crucible. If it is then rapidly cooled in water (Chap. VIII., note 17a), it gives a uniform crystalline mass of carbide of sp. gr. 7·07, which readily rusts in air; its powder burns in oxygen (see note 9). Crystals of carbide embedded in steel are called ‘cementite.’

⁶ The primitive methods of iron manufacture were conducted by intermittent processes in hearths resembling smith’s fires. As evidenced by the uninterrupted action of the steam boiler, or the process of lime burning, and the continuous preparation and condensation of sulphuric acid or the uninterrupted smelting of iron, every industrial process becomes increasingly profitable and complete under the condition of the continuous action, as far as possible, of all agencies concerned in the production. This method lessens the cost of labour, simplifies the supervision of the work, renders the product uniform, and frequently introduces a very great economy in the expenditure of fuel and at the same time presents the simplicity and perfection of an equilibrated system. Hence every manufacturing operation should be a continuous one.

bottom of the furnace above the heavier cast iron. This is effected by mixing certain **fluxes** with the ore and charcoal. A flux is a substance which, when mixed with the foreign matter of the ore, forms a fusible vitreous mass or slag. The flux used for silica is limestone with clay; for limestone a definite quantity of silica is used, the best procedure having been arrived at by experiment and by long practice in iron smelting and other metallurgical processes.⁷

Thus the following materials have to be introduced into the furnace where the smelting of the iron ore is carried on: (1) the iron ore, composed of oxide of iron and foreign matter; (2) the flux required to form a fusible slag with the foreign matter; (3) the carbon which is necessary (*a*) for reducing, (*b*) for combining with the reduced iron to form cast iron, (*c*) principally for the purpose of combustion and the heat generated thereby, necessary not only for reducing the iron and transforming it into cast iron, but also for melting the slag, as well as the cast iron—and (4) the air necessary for the combustion of the charcoal. The air is introduced after a preparatory heating in order to economise fuel and to obtain the highest temperature. The air is forced in under pressure by means of a special blast arrangement. This permits of an exact regulation of the heat and rate of smelting. All these component parts necessary for the smelting of iron must be contained in a vertical, that is, **shaft furnace**, which at the base must have a receptacle for the accumulation of the slag and cast iron formed, in order that the operation may proceed without interruption. The walls of such a furnace ought to be built of fire-proof materials if it be designed to serve for the continuous production of cast iron by charging the ore, fuel, and flux into the mouth of the furnace, forcing a blast of air into the lower part, and running out the molten iron and slag from

⁷ The composition of slag suitable for iron smelting most often approaches the following: 50 to 60 per cent. SiO_2 , 5 to 20 Al_2O_3 , the rest of the mass consisting of MgO , CaO , MnO , FeO . Thus the most fusible slag (according to the observations of Bodeman) contains the alloy $\text{Al}_2\text{O}_3, 4\text{CaO}, 7\text{SiO}_2$. On altering the quantity of magnesia and lime, and especially of the alkalis (which increases the fusibility) and of silica (which decreases it), the temperature of fusion changes with the relation between the total quantity of oxygen and that in the silica. Slags of the composition RO, SiO_2 are easily fusible, have a vitreous appearance, and are very common. Basic slags approach the composition $2\text{RO}, \text{SiO}_2$. Hence, knowing the composition and quantity of the foreign matter in the ore, it is at once easy to find the quantity and quality of the flux which must be added to form a suitable slag. The smelting of iron is rendered more complex by the fact that the silica, SiO_2 , which enters into the slag and fluxes is capable of forming a slag with the iron oxides. In order that the least quantity of iron may pass into the slag, it is necessary for it to be reduced before the temperature is attained at which the slags are formed (about 1000°), which is effected by reducing the iron, not with charcoal itself, but with carbonic oxide. From this it will be understood how the progress of the whole treatment may be judged by the properties of the slags. Details of this complicated and well-studied subject will be found in works on metallurgy.

below. The whole operation is conducted in furnaces known as **blast furnaces**.⁸ The annexed illustrations, figs. 103 and 104 (the latter taken

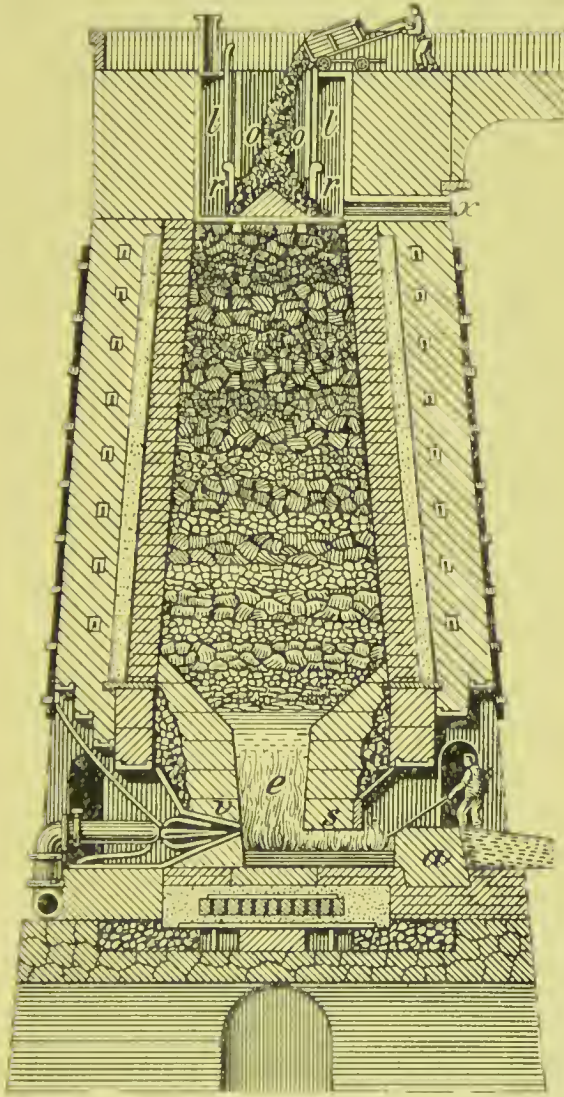


FIG. 103.—Vertical section of blast furnace. Scale 1 : 200. *x* is the pipe by which the furnace gases are drawn off. On the cylinder, *oo*, which does not reach the cone below it, another cylinder, *rr*, moves by means of the rods *ll*; *rr* is kept pushed down except when the furnace is being charged, when it is raised. *e* shows the hearth of the furnace, and *v* one of the *tuyères* through which the hot blast is introduced. Between *s* and *a* is an opening for letting the molten cast iron and slag run out.

* The section of a blast furnace is represented by two truncated cones joined at their bases, the upper cone being longer than the lower one; the lower cone is terminated by the hearth, or almost cylindrical cavity in which the cast iron and slag collect, one side being provided with apertures for drawing off the iron and slag. The air is blown into the blast furnace through special pipes situated over the hearth, as shown in the sections. The air previously passes through a series of cast-iron pipes, heated by the combustion of the carbonic oxide obtained from the upper parts of the furnace, where it is formed as in a 'gas-producer.' The amount of combustible blast furnace gases

of large dimensions, varying from fifty to ninety feet in height. They are sometimes built against rising ground in order to afford easy access to the top where the ore, flux, and charcoal or coke are charged.^{8a}

The **cast iron** formed in blast furnaces is not always of the same quality. When slowly cooled it is soft, has a grey colour, and is not

and steel. The chief producers are the United States (about 15 million tons a year) and England (about 9 million tons a year); Russia yields about $2\frac{1}{2}$ million tons a year. About a million tons of pyrites are produced by the world in a year.

^{8a} In order to more thoroughly grasp the chemical process which takes place in blast furnaces, it is necessary to follow the course of the material charged in at the top and that of the air passing through the furnace. From 50 to 200 parts of carbon are expended on 100 parts of iron. The ore, flux, and coke are charged into the top of the furnace, in layers, as the cast iron formed in the lower parts flows down to the bottom and so causes the whole contents of the furnace to subside, thus forming an empty space at the top, which is again filled up with the afore-mentioned mixture. During its downward course this mixture is subjected to increasing heat. This rise of temperature first drives off the moisture of the ore mixture and then leads to the formation of the products of the dry distillation of coal or charcoal. Little by little the subsiding mass attains a temperature at which the heated carbon reacts with the carbonic anhydride passing upwards through the furnace and transforms it into carbonic oxide. This is the reason why carbonic anhydride is not evolved from the furnace, but chiefly carbonic oxide. As regards the ore itself, on being heated to about 600° to 800° it is reduced at the expense of the **carbonic oxide** and not by carbon itself (see note 5); thus, $\text{Fe}_2\text{O}_3 + 3\text{CO} = \text{Fe}_3 + 3\text{CO}_2$. The reduced iron, on further subsidence and contact with carbon, forms cast iron, which flows to the bottom of the furnace. In these lower layers, where the temperature is highest (about 1300°), the foreign matter of the ore finally forms slag, which is also fusible, with the aid of fluxes. The air blown in from below, through the so-called *tuyères*, encounters carbon in the lower layers of the furnace, and burns it, converting it into carbonic anhydride. It is evident that this develops the highest temperature in these lower layers of the furnace, because here the combustion of the carbon is effected by heated air. The carbonic acid formed rises higher, encounters incandescent carbon, and forms with it carbonic oxide. This heated carbonic oxide acts as a reducing agent on the iron ore, and is reconverted by it into carbonic anhydride; this gas meets with more carbon, and again forms carbonic oxide, which again acts as a reducing agent. The final transformation of the carbonic anhydride into carbonic oxide is effected in those parts of the furnace where the reduction of the oxides of iron does not take place, but where the temperature is still high enough to reduce the carbonic anhydride. The ascending mixture of carbonic oxide and nitrogen, CO_2 , &c., is then withdrawn through special lateral apertures formed in the upper cold parts of the furnace walls, and is conducted through pipes to the furnaces used for heating the air, and also to other furnaces used for the further processes of iron manufacture, and even (since the close of the nineteenth century) to gas engines. The fuel of blast furnaces consists of wood charcoal (this is the most expensive material, but the pig iron produced is the purest, because charcoal does not contain any sulphur, while coke does), anthracite (for instance, in Pennsylvania, and in Russia at Pastoukhoff's works in the Don district), coke, coal, and even wood and peat. It must be borne in mind that the utilisation of naphtha and naphtha refuse would probably give very profitable results in metallurgical processes.

The process just described is accompanied by a series of other processes. Thus, for instance, in the blast furnace a considerable quantity of cyanogen compounds is formed. This takes place because the nitrogen of the air blast comes into contact with incandescent carbon and various alkaline matters contained in the foreign matter of the ores.

completely soluble in acids. When treated with acids a residue of graphite remains ; it is known as **grey** or soft cast iron. This is the general form of the ordinary cast iron used for casting various objects, because in this state it is not so brittle as in the shape of **white cast iron**, which does not leave particles of graphite when dissolved, but yields its carbon in the form of hydrocarbons. This white cast iron is characterised by its whitish-grey colour, dull lustre, the crystalline structure of its fracture (more homogeneous than that of grey iron), and such hardness that a file will hardly cut it. When white cast iron is produced (from manganese ore) at high temperatures (and with an excess of lime), and contains little sulphur and silica but a considerable amount of carbon (as much as 5 per cent.), it acquires a coarse crystalline structure which increases in proportion to the amount of manganese, and it is then known under the name of 'spiegeleisen' (and 'ferromanganese').⁹

Cast iron is a material which is suitable either for direct application for casting in moulds or for working up into **wrought iron** and **steel**. The latter principally differ from cast iron in their containing less carbon—thus, steel contains from 1 to 0·5 per cent. of carbon and far less silicon and manganese than cast iron ; wrought iron does not generally contain more than 0·25 per cent. of carbon and not more than 0·25 per cent. of the other impurities. Thus the essence of the work-

⁹ The specific gravity of white cast iron is about 7·5, and that of grey cast iron, 7·0. Grey cast iron generally contains less manganese and more silica than white, but both contain from 2 to 3 per cent. of carbon. The difference between the varieties of cast iron depends on the condition of the carbon which enters into the composition of the iron. In white cast iron the carbon is in combination with the iron, as the compound CFe_3 (note 5). Abel and Osmond and others extracted this compound, which is sometimes called 'carbide,' from tempered steel, which stands to unannealed steel as white cast iron does to grey. In any case the compound of the iron and carbon in white cast iron is chemically very unstable, because when slowly cooled it decomposes, with separation of graphite, just as a solution when slowly cooled yields a portion of the substance dissolved. The separation of carbon in the form of graphite on the conversion of white cast iron into grey is never complete, however slowly the separation be carried on ; part of the carbon remains in combination with the iron in the same state in which it exists in white cast iron. Hence when grey cast iron is treated with acids, the whole of the carbon does not remain in the form of graphite, but a part of it is separated as hydrocarbons. It is sufficient to re-melt grey cast iron and cool it quickly to re-transform it into white cast iron. It is not carbon alone that influences the properties of cast iron ; when it contains a considerable amount of sulphur, cast iron remains white, even after having been slowly cooled. The same is observed in cast iron very rich in manganese (5 to 7 per cent.), and in this latter case the fracture is very distinctly crystalline and brilliant. When cast iron contains a large amount of manganese, the quantity of carbon may also be increased. Grey cast iron not having a uniform structure is much more liable to various changes than dense and more uniform white cast iron. White cast iron is used not only for conversion into wrought iron and steel, but also in those cases where great hardness is required, although it be accompanied by a certain brittleness, for instance, for making rollers, ploughshares, &c.

ing-up of cast iron into steel and wrought iron consists in the removal of the greater part of the carbon and other elements, S, P, Mn, Si, &c. This is effected by means of oxidation, because the oxygen of the atmosphere, oxidising the iron at a high temperature, forms with it solid oxides; and the latter, coming into contact with the carbon contained in the cast iron, are deoxidised, forming wrought iron and carbonic oxide, which is evolved from the mass in a gaseous form. It is evident that the oxidation must be carried on with a molten mass in a state of agitation, so that the oxygen of the air may be brought into contact with the whole mass of carbon contained in the cast iron, or else the operation is effected by means of the addition of oxygen compounds of iron (oxides, ores, as in Martin's process). Cast iron melts much more easily than wrought iron and steel, and therefore, as the carbon separates, the mass in the furnace (in puddling) or hearth (in the bloomery process) becomes more and more solid; moreover, the degree of hardness forms, to a certain extent, a measure of the amount of carbon separated, and the operation may terminate in the formation of either steel or wrought iron.¹⁰ In any case, the iron used for

¹⁰ This direct process of separating the carbon from cast iron is termed **puddling**. It is conducted in reverberatory furnaces. The cast iron is placed on the bed of the furnace and melted; through a special aperture, the puddler stirs up the oxidising mass of cast iron, pressing the oxides into the molten iron. This resembles kneading dough, and the process introduced into England became known as puddling. It is evident that the puddled mass, or bloom, is a heterogeneous substance obtained by mixing, and hence one part of the mass will still be rich in carbon, another will be poor, some parts will contain oxide not reduced, &c. The further treatment of the puddled mass consists in hammering and drawing it out into flat pieces, which on being hammered become more homogeneous, and when several pieces are welded together and again hammered out a still more homogeneous mass is obtained. The quality of the steel and iron thus formed depends principally on their uniformity. In order to obtain a more homogeneous metal for manufacturing articles out of steel, it is drawn into thin rods, which are tied together in bundles and then again hammered out. As an example of what may be attained in this direction, imitation Damascus steel may be cited; it consists of twisted and plaited wire, which is then hammered into a dense mass. (Real damascened wootz steel may be made by melting a mixture of the best iron with graphite ($\frac{1}{12}$) and iron rust; the article is then corroded with acid, and the carbon remains in the form of a pattern.)

Steel and wrought iron are manufactured from cast iron by puddling. They were formerly obtained by the **bloomery process**, carried out in a fire similar to a blacksmith's forge, fed with charcoal and provided with a blast; a pig of cast iron is gradually pushed into the fire, and portions of it melt and fall to the bottom of the hearth, coming into contact with an air blast, and are thus oxidised. The bloom thus formed is then squeezed and hammered. It is evident that this process is only available when the charcoal used in the fire does not contain any foreign matter which might injure the quality of the iron or steel—for instance, sulphur or phosphorus. Only wood charcoal may be used with impunity, from which it follows that this process can only be carried on where the manufacture of iron can be conducted with this fuel. Coal and coke contain the above-mentioned impurities, and would therefore produce iron of a brittle nature, and thus it would be necessary to have recourse to puddling, the fuel being burnt on a special hearth, separate from the cast iron, whereby the impurities of the fuel do not come into

industrial purposes contains impurities. Chemically pure iron may be obtained by precipitating iron from a solution (a mixture of ferrous

contact with it. The manufacture of steel from cast iron may also be conducted in fires; but, in addition to this, it is also now prepared by many other methods. One of the long-known processes is called **cementation**, by which steel is prepared from wrought iron but not from cast iron. For this process strips of iron are heated to redness for a considerable time while immersed in powdered charcoal; during this operation the iron at the surface combines with the charcoal, which, however, does not penetrate; after this the iron strips are re-forged, drawn out again, and cemented anew, this process being repeated until a steel of the desired quality is formed—that is, containing the requisite proportion of carbon. The **Bessemer** process occupies the front rank among the newer methods

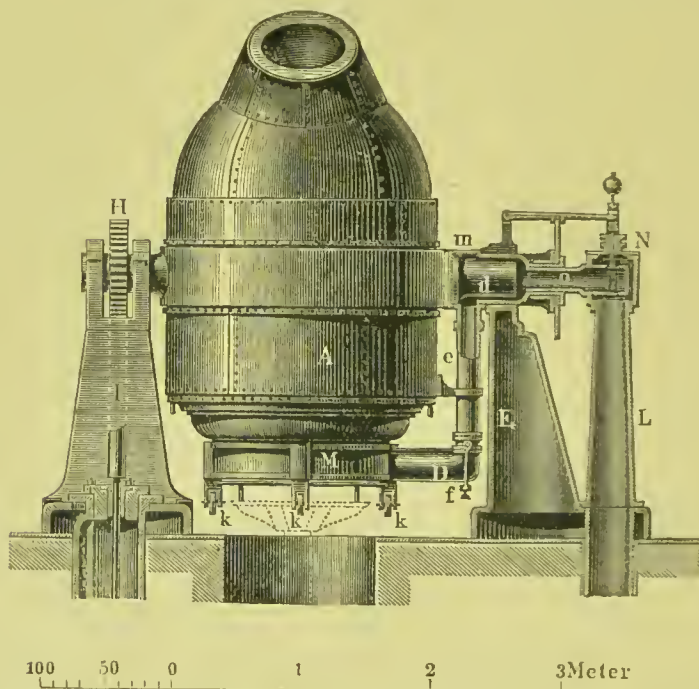


FIG. 105—Bessemer converter, constructed of iron plate and lined with ganister. The air is carried by the tubes, L, O, D, to the bottom, M, from which it passes by a number of holes into the converter. The converter is rotated on the trunnion *d* by means of the rack and pinion H, when it is required either to receive molten east iron from the melting furnaces or to pour out the steel.

(since 1855); it is so called from the name of its inventor. This process consists in running melted cast iron into converters (holding about 6 tons of east iron)—that is, egg-shaped receivers, fig. 105, capable of revolving on trunnions (in order to charge in the east iron and discharge the steel), and forcing a stream of air through small apertures at a considerable pressure. Combustion of the iron and carbon (Mn, &c.) at a high temperature then takes place, resulting from the bubbles of oxygen thus penetrating the mass of the cast iron. The carbon, however, burns to a greater extent than the iron, and a mass is therefore obtained which is much poorer in carbon than cast iron. As the combustion proceeds rapidly, the temperature rises to such an extent that even the wrought iron which may be formed remains in a molten condition, whilst the steel, being more fusible than the wrought iron, remains very liquid. In half an hour the mass is ready. The purest possible cast iron is used in the Bessemer process, because sulphur and phosphorus do not burn out like carbon, silicon, and manganese.

sulphate with magnesium sulphate or ammonium chloride) by the prolonged action of a feeble galvanic current; the iron may be then

The presence of manganese enables the sulphur to be removed with the slag, and the presence of lime or magnesia, which are introduced into the lining of the converter, facilitates the removal of the phosphorus. This basic Bessemer process, or **Thomas-Gilchrist process**, introduced about 1880, enables ores containing a considerable amount of phosphorus, which had hitherto only been used for cast iron, to be used for making wrought iron and steel. Naturally the greatest uniformity will be obtained by re-melting the metal. Steel is re-melted, in small wind furnaces, in masses not exceeding 30 kilos; a liquid metal is formed, which may be cast in moulds. A mixture of wrought and cast iron is often used for making cast steel (the addition of a small amount of metallic Al improves the homogeneity of the castings by facilitating the passage of the impurities into slag). Large steel castings are made by simultaneous fusion in several furnaces and crucibles; in this way, castings up to 80 tons or more, such as large ordnance, may be made. This molten, and therefore homogeneous, steel is called **cast steel**. In the last quarter of the nineteenth century **Martin's process** for the manufacture of steel has come largely into use; it was invented in France about 1860, and with the use of regenerative furnaces it enables large quantities of cast steel to be made at a time. It is based on the melting of cast iron with iron oxides and iron itself—for instance, pure ores, scrap, &c. There the carbon of the cast iron and the oxygen of the oxide form carbonic oxide, and the carbon therefore burns out, and thus cast steel is obtained from cast iron, providing, naturally, that there is a requisite proportion and corresponding degree of heat. The advantage of this process is that not only do the carbon, silicon, and manganese, but also a great part of the sulphur and phosphorus of the cast iron burn out at the expense of the oxygen of the iron oxides. The manufacture of steel and its applications for rails, armour plate, guns, boilers, &c., have developed to an enormous extent, thanks to the invention of cheap processes for the manufacture of large masses of homogeneous cast steel. Wrought iron may also be melted, but the heat of a blast furnace is insufficient for this. It melts easily in the oxyhydrogen flame and in the regenerator furnace (Chap. IX., note 22). It may be obtained in a molten state directly from cast iron, if the latter be melted with nitre and sufficiently stirred up. Considerable oxidation then takes place inside the mass of cast iron, and the temperature rises to such an extent that the wrought iron formed remains liquid. Iron may also be obtained direct in a fused state by burning a mixture of Fe_2O_3 and aluminium powder (thermite, Chap. III., note 42). A method is also known for obtaining wrought iron directly from rich iron ores by the action of carbonic oxide; the wrought iron is then formed as a spongy mass (which forms an excellent filter for purifying water), and may be worked up into wrought iron or steel either by forging or by dissolving in molten cast iron.

Everybody is more or less familiar with the **difference in the properties of steel and wrought iron**. Iron is remarkable for its softness, pliability, and small elasticity, whilst steel may be characterised by its capability of attaining elasticity and hardness if it be cooled suddenly after having been heated to a definite temperature, or, as it is termed, *tempered*. But if tempered steel be re-heated and slowly cooled, it becomes as soft as wrought iron, and can then be cut with the file and forged, and in general can be made to assume any shape, like wrought iron. In this soft condition it is called *annealed steel*. The transition from tempered to annealed steel thus takes place in a similar way to the transition from white to grey cast iron. Steel, when homogeneous, has considerable lustre, and such a fine granular structure that it takes a very high polish. Its fracture clearly shows the granular nature of its structure. The possibility of tempering steel enables it to be used for making all kinds of cutting instruments, because annealed steel can be forged, turned, drawn (under rollers, for instance, for making rails, bars, &c.), filed, &c., and it may then be tempered, ground, and polished. The method and temperature of tempering and annealing steel determine its hardness and other qualities. Steel is generally tempered to the required degree of hardness in the following manner: It is first strongly heated (for instance, up to 600°) and then plunged into water—that

obtained as a dense mass. This method (Böttcher and Klein) gives, as R. Lenz showed, iron containing occluded hydrogen, which is disengaged on heating, after which it becomes soft. If pure ferric hydroxide, which is easily prepared by the precipitation of solutions of ferric salts by means of ammonia, be heated in a stream of hydrogen, it forms, first of all, a dull-black powder which takes fire in air (pyrophoric is, hardened by rapid cooling (it then becomes as brittle as glass). It is then heated until the surface assumes a certain colour, and finally cooled either quickly or slowly. When steel is heated up to 220° , its surface acquires a yellow colour (surgical instruments): it first of all becomes straw-coloured (razors, &c.), and then gold-coloured: then at a temperature of 250° it becomes brown (scissors), then red, then light blue at 285° (springs), indigo at 300° (files), and finally sea-green at about 340° . These colours are only the tints of thin films, like the hues of soap bubbles, and appear on the steel because a thin layer of oxides is formed over its surface. Steel rusts more slowly than wrought iron, and is more soluble in acids than cast iron, but less so than wrought iron. Its specific gravity is about 7.6 to 7.9.

The formation and structure of steel, the effect of different impurities on it, and its variation under different circumstances now form one of the best investigated portions of metallurgy, and this would not be the place to discuss it. I shall only remark that now, when fused iron is obtained in the Siemens furnace or converter with as much ease as steel, the distinction between iron and steel (for the cast or fused metal) has lost its former sense and significance, although it should be still retained in speaking of the metal which has not been subjected to fusion. And as the properties of the metal (generally called steel) vary in dependence upon the amount of carbon in it, I give the following classification, due to Cockerell (1878): (1) *Very mild steel* contains from 0.05 to 0.20 per cent. of carbon, breaks with a weight of 40 to 50 kilos per square millimetre, and has an extension of 20 to 30 per cent.; it may be welded, like wrought iron, but cannot be tempered; it is used in sheets for boilers, armour plate and bridges, nails, rivets, &c., as a substitute for wrought iron; (2) *mild steel*, from 0.20 to 0.35 per cent. of carbon: resistance to tension 50 to 60 kilos, extension 15 to 20 per cent., not easily welded, and tempers badly; used for axles, rails, and railway tyres, for cannons and guns, and for parts of machines destined to resist bending and torsion; (3) *hard steel*, carbon 0.35 to 0.50 per cent., breaking weight 60 to 70 kilos per square millimetre, extension 10 to 15 per cent., cannot be welded, takes a temper; used for rails, all kinds of springs, swords, parts of machinery in motion subjected to friction, spindles of looms, hammers, spades, hoes, &c.; (4) *very hard steel*, carbon 0.5 to 0.65 per cent., tensile breaking weight 70 to 80 kilos, extension 5 to 10 per cent., does not weld, but tempers easily; used for small springs, saws, files, knives, and similar instruments.

The variations in the properties of iron and steel depend on the impurities which they contain. In general, the iron used in the arts still contains carbon and always a certain quantity of silicon, manganese, sulphur, phosphorus, &c. A variety in the proportion of these component parts changes the quality of the iron. In addition to this the change which soft wrought iron, having a fibrous structure, undergoes when subjected to repeated blows and vibrations is considerable; it then becomes granular and brittle. This explains to a certain degree the want of stability of some iron objects—such as truck axles, which must be renewed after a certain term of service, as otherwise they become brittle. It is evident that there are innumerable intermediate transitions from wrought iron to steel and cast iron.

I may add that the Urals, Donetz district, and the Kusnetz coal-fields of Western Siberia offer the greatest advantages for the development of a vast iron industry, because these localities not only contain enormous supplies of excellent iron ore, but also coal, which is necessary for smelting it. The Ural district with its cheap charcoal is best suited for the production of the higher grades of steel, as is shown in my work, *The Iron Industry of the Urals in 1899*, written after my journey to the Urals.

iron) and then a grey powder of pure iron which does not burn in the air. The powdery substance first obtained is an iron suboxide; when thrown into the air it ignites, forming the oxide Fe_3O_4 . If a small quantity of the pure powdery iron be fused in the oxyhydrogen flame (with an excess of oxygen) in a piece of lime and mixed with powdered glass, pure molten iron will be formed, because in the oxyhydrogen flame iron melts and burns, but the substances mixed with the iron oxidise first. Pure iron has a silvery white colour and a specific gravity of 7.84; it melts at a temperature higher than the melting-points of silver, gold, nickel, and steel, viz., about 1400° – 1500° and below the melting-point of platinum (1750°).¹¹ But pure iron becomes soft at a temperature considerably below that at which it melts, and may then be easily forged, welded, and rolled or drawn into sheets and wire.^{11a} Pure iron may be rolled into an exceedingly thin sheet, weighing less than a sheet of ordinary paper of the same size. This ductility is the most important property of iron in all its forms, and is most marked with sheet iron, and least so with cast iron, whose ductility, compared with that of wrought iron, is small.¹²

¹¹ According to information supplied by A. T. Skinder's experiments at the Oboukoff Steel Works, 140 volumes of liquid molten steel give 128 volumes of solid metal. By means of a galvanic current of great intensity and using dense charecoal as one electrode and iron as the other, Bernadoss welded iron and fused holes through sheet iron. Soft wrought iron, like steel and soft malleable cast iron, may be easily melted in Siemens's regenerative furnaces, and in furnaces heated with naphtha.

^{11a} Gore (1869), Tait, Barret, Tchernoff, Osmond, and others observed that at a temperature approaching 600° —that is, between dark and bright-red heat—all kinds of wrought iron undergo a peculiar change called **recalcence**, i.e., a spontaneous rise of temperature. If iron be considerably heated and allowed to cool, it may be observed that at this temperature the cooling stops—that is, latent heat is disengaged, corresponding with a change in condition. The specific heat, electrical conductivity, magnetic and other properties then also change. In tempering, and also in annealing, &c., the temperature of recalcence must not be reached. It is evident that a change of the internal condition is here encountered, exactly similar to the transition from a solid to a liquid, although there is no evident physical change.

¹² The particles of steel are linked together or connected more closely than those of the other metals; this is shown by the fact that it only **breaks** with a tensile stress of 50–80 kilos per sq. mm., whilst wrought iron only withstands about 30 kilos, cast iron 10, copper 35, silver 23, platinum 30, and wood 8. The elasticity of iron, steel, and other metals is expressed by the so-called **coefficient of elasticity**. Let a rod be taken whose length is L ; if a weight, P , be hung from the extremity of it, it will lengthen by l . The less it lengthens under other equal conditions, the more elastic the material, if it resumes its original length when the weight is removed. It has been shown by experiment that the increase in length, l , due to elasticity, is directly proportional to the length L and the weight P , and inversely proportional to the area of cross-section, but changes with the material. The coefficient of elasticity expresses that weight (in kilos per sq. mm.) under which a rod having a cross section taken as 1 (we take 1 sq. mm.) acquires double the length by tension. Naturally in practice materials do not withstand such a lengthening, but under a certain weight they attain a limit of elasticity, i.e., they stretch permanently (undergo deformation). Neglecting fractions (as the elasticity of metals

The chemical properties of iron have been already repeatedly mentioned in preceding chapters. Iron rusts in air at the ordinary temperature—that is to say, it becomes covered with a layer of iron oxides. Here, without doubt, the moisture of the air plays a part, because in dry air iron does not oxidise at all, and also because, more particularly, ammonia is always found in iron rust; the ammonia must arise from the action of the hydrogen of the water, at the moment of its separation, on the nitrogen of the air. Highly polished steel does not rust nearly so readily, but if moistened with water, it easily becomes coated with rust. As rust depends on the access of moisture, iron may be preserved from rust by coating it with substances which prevent the moisture coming into contact with it. Thus arises the practice of covering iron objects with paraffin,¹³ varnish, oil, paints, or enamelling it with a glassy-looking flux possessing the same coefficient of expansion as iron, or with a dense scoria (formed by the heat of superheated steam), or with a compact coating of various metals. Wrought iron (both as sheet iron and in other forms), cast iron, and steel are often coated with tin, copper, lead, nickel, and similar metals, which prevent contact with the air. These metals preserve iron very effectually from rust if they form a perfectly compact surface; but in those places where the iron becomes exposed, either accidentally or from wear, rust appears much more quickly than on a uniform iron surface, because towards these metals (and also towards the rust) the iron will then behave as an electro-positive pole in a galvanic couple, and will hence attract oxygen. A coating of zinc does not produce this inconvenience, because iron is electro-negative with reference to zinc, in consequence of which galvanised iron does not easily rust, and even an iron boiler containing lumps of zinc rusts less than one without zinc.¹⁴ Iron oxidises at a high temperature, forming **iron scale**, Fe_3O_4 , composed of ferrous and ferric oxides, and, as has been seen, decomposes water and acids with the evolution of hydrogen. It is also capable of decomposing salts and oxides of other metals, which property is applied in the arts

varies not only with the temperature, but also with forging, purity, &c.), the coefficient of elasticity is for steel and iron 20,000; for copper and brass 10,000; for silver 7,000; for glass 6,000; for lead 2,000; and for wood 1,200.

¹³ Paraffin is one of the best preservatives for iron against oxidation in the air. I found this by experiments about 1860, and immediately published the fact. This method is now very generally applied.

¹⁴ See Chapter XVIII., note 34a. Based on the rapid oxidation of iron and its increase in volume in the presence of water and salts of ammonium, a packing is used for water mains and steam pipes which is tightly hammered into the socket-joints. This packing consists of a mixture of iron filings and a small quantity of sal-ammoniac (and sulphur) moistened with water; after a certain lapse of time, especially after the pipes have been used, this mass swells to such an extent that it hermetically seals the joints of the pipes.

for the extraction of copper, silver, lead, tin, &c. For this reason iron is soluble in the solutions of many salts—for instance, in cupric sulphate, with precipitation of copper and formation of ferrous sulphate.¹⁵ When iron **acts on acids** it always **forms compounds**, FeX_2 —that is, corresponding to the suboxide FeO —answering to magnesium compounds, and hence two atoms of hydrogen are replaced by one of iron. Strongly oxidising acids, like nitric acid, may transform the ferrous salt which is forming, into the higher degree of oxidation or the ferric salt (corresponding with the sesquioxide, Fe_2O_3), but this is a secondary reaction. Iron, although easily soluble in dilute nitric acid, loses this property when plunged into strong fuming nitric acid; after this operation it even loses the property of solubility in other acids until the external coating formed by the action of the strong nitric acid is mechanically removed. This condition of iron is termed the passive state. **The passive condition** of iron depends on the formation, on its surface, of a coating of oxide, due to the iron being acted on by the lower oxides of nitrogen contained in the fuming nitric acid.¹⁶ Strong nitric acid which does not contain these lower oxides, does not render iron passive, but it is only necessary to add some alcohol or other reducing agent which forms these lower oxides in the nitric acid, and the iron will assume the passive state.

Iron readily combines with non-metals—for instance, with chlorine, iodine, bromine, sulphur, and even with phosphorus and carbon—and with metals, although it fuses with difficulty. Mn, Cr, W, Cu, and other metals combine with and dissolve in Fe, and in so doing modify its properties. On the other hand Fe greatly alters the properties of Cu, Al, &c., when dissolved in them, although no definite compounds of them are known, owing to the difficulties presented by their investigation. Mercury, which acts on most metals, does not act directly on iron, and the **iron amalgam**, or solution of iron in mercury, which is used for electrical machines, is only obtained in a particular way—namely, with the co-operation of a sodium amalgam, in which the iron

¹⁵ Here, however, a ferric salt may also be formed (when all the iron has dissolved and the cupric salt is still in excess), because the cupric salts are reduced by ferrous salts. Cast iron is also dissolved.

¹⁶ Powdery reduced iron is passive with regard to nitric acid of a specific gravity of 1.37, but when heated the acid acts on it. This passiveness disappears in the magnetic field. Saint-Edme attributes the passiveness of iron (and nickel) to the formation of nitride of iron on the surface of the metal, because he observed that when heated in dry hydrogen, ammonia is evolved by passive iron.

Remsen observed that if a strip of iron is immersed in acid and placed in the magnetic field, it is dissolved principally at its middle part—that is, the acid acts more feebly at the poles. According to Étard (1891), strong nitric acid dissolves iron in making it passive, although the action is a very slow one.

dissolves and by means of which it is reduced from solutions of its salts.

When iron acts on acids it forms ferrous salts of the type FeX_2 , and in the presence of air and oxidising agents these change by degrees into ferric salts of the type FeX_3 . The faculty of passing from the ferrous to the ferric state is particularly developed in ferrous hydroxide. If sodium hydroxide is added to a solution of ferrous sulphate or green vitriol, FeSO_4 ,¹⁷ a white precipitate of **ferrous hydroxide**, $\text{Fe}(\text{OH})_2$, is obtained; but on exposure to the air, even under water, it turns green, becomes grey, and finally brown, owing to the oxidation which it undergoes. Ferrous hydroxide is very sparingly soluble in water; its solution has, however, a distinct alkaline reaction, which is due to its being a fairly energetic basic oxide. In any case, ferrous oxide is far more energetic than ferric oxide, so that if ammonia be added to a solution containing a mixture of a ferrous and a ferric salt, at first ferric hydroxide only will be precipitated. If barium carbonate, BaCO_3 , is shaken up in the cold with ferrous salts, it does not precipitate them—that is, does not change them into ferrous carbonate; but it completely

¹⁷ **Iron vitriol** or **green vitriol**, sulphate of iron or ferrous sulphate, generally crystallises from solutions, like magnesium sulphate, with seven molecules of water, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. This salt is not only formed by the action of iron on sulphuric acid, but also by the action of moisture and air on iron pyrites, especially when these are previously roasted ($\text{FeS}_2 + \text{O}_2 = \text{FeS} + \text{SO}_2$), and in this condition it easily absorbs the oxygen of damp air ($\text{FeS} + \text{O}_2 = \text{FeSO}_4$). Green vitriol is obtained in many processes as a by-product. Like all the ferrous salts, it has a pale-greenish colour, hardly perceptible in solution. If it be desired to preserve it without change—that is, so as not to contain ferric compounds—it is necessary to keep it hermetically sealed. This is best done by expelling the air by means of sulphurous anhydride; the SO_2 removes oxygen from any ferric compounds which might be formed, and is itself changed into sulphuric acid, so that the oxidation of the ferrous compound does not take place in its presence. Unless these precautions are taken, green vitriol turns brown, changing partly into the ferric salt. When turned brown, it is not completely soluble in water, because during its oxidation a certain amount of free insoluble ferric oxide is formed: $6\text{FeSO}_4 + \text{O}_2 = 2\text{Fe}_2(\text{SO}_4)_3 + \text{Fe}_2\text{O}_3$. In order to cleanse such mixed green vitriol from the oxide, it is necessary to add some sulphuric acid and iron and boil the mixture; the ferric salt is then transformed into the ferrous state: $\text{Fe}_2(\text{SO}_4)_3 + \text{Fe} = 3\text{FeSO}_4$.

Green vitriol is used for the manufacture of Nordhausen sulphuric acid (Chap. XX.), for preparing ferric oxide, in many dye works (for preparing the indigo vats and reducing blue indigo to white), and in many other processes; it is also a very good disinfectant, and is the cheapest salt from which other compounds of iron may be obtained.

The other ferrous salts (excepting the yellow prussiate, which will be mentioned later) are but little used, and it is therefore unnecessary to dwell upon them. We shall only mention **ferrous chloride**, which, in the crystalline state, has the composition $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$. It is easily prepared; for instance, by the action of hydrochloric acid on iron, and in the anhydrous state by the action of hydrochloric acid gas on metallic iron at a red heat. The anhydrous ferrous chloride then volatilises in the form of colourless cubic crystals. Ferrous oxalate (or the double potassium salt) acts as a powerful reducing agent, and is frequently employed in photography (as a developer).

separates all the iron from ferric salts in the cold, according to the equation : $\text{Fe}_2\text{Cl}_6 + 3\text{BaCO}_3 + 3\text{H}_2\text{O} = \text{Fe}_2\text{O}_3 + 3\text{H}_2\text{O} + 3\text{BaCl}_2 + 3\text{CO}_2$. If ferrous hydroxide is boiled with a solution of potash, the water is decomposed, hydrogen is evolved, and the ferrous hydroxide oxidised. The ferrous salts are in all respects similar to those of magnesium and zinc ; they are isomorphous with them, but differ from them in that the ferrous hydroxide is not soluble either in aqueous potash or ammonia. In the presence of an excess of ammonium salts, however, a certain proportion of the iron is not precipitated by alkalies and alkali carbonates, which fact points to the formation of double ammonium salts.¹⁸ The ferrous salts have a dull **greenish** colour, and form solutions also of a pale-green colour, whilst the ferric salts have a **brown** or reddish-brown colour. The ferrous salts, being capable of oxidation, form active reducing agents—for instance, under their action gold chloride, AuCl_3 , deposits metallic gold, nitric acid is transformed into lower oxides, and the higher oxides of manganese also pass into the lower forms of oxidation. All these reactions take place with especial ease in the presence of an excess of acid. This depends on the fact that the ferrous oxide, FeO (or salt), acting as a reducing agent, turns into ferric oxide, Fe_2O_3 (or salt), and in the ferric state requires more acid for the formation of a normal salt than in the ferrous condition. Thus, in the normal ferrous sulphate, FeSO_4 , there is one equivalent of iron to one equivalent of sulphur (in the sulphuric radicle) but in the neutral ferric salt, $\text{Fe}_2(\text{SO}_4)_3$, there is one equivalent of iron to one and a half of sulphur in the form of the elements of sulphuric acid.¹⁹

¹⁸ Ferrous sulphate, like magnesium sulphate, readily forms double salts—for instance, $(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}$. This salt does not oxidise in air so rapidly as green vitriol and is therefore used for standardising KMnO_4 solutions.

¹⁹ The transformation of ferrous oxide into ferric oxide is not completely effected in air, as then only a part of the suboxide is converted into ferric oxide. Under these circumstances the so-called **magnetic oxide** of iron is generally produced, which contains molecular proportions of the suboxide and oxide—namely, $\text{FeO} \cdot \text{Fe}_2\text{O}_3 = \text{Fe}_3\text{O}_4$. This substance, as already mentioned, is found in nature and in iron scale. It is also formed when most ferrous and ferric salts are heated in air ; thus, for instance, when ferrous carbonate, FeCO_3 (either native or as the precipitate given by soda in a solution of FeX_2), is heated it loses the elements of carbonic anhydride, and magnetic oxide remains. This oxide of iron is attracted by a magnet, and is on this account called magnetic oxide, although it does not always show magnetic properties. If magnetic oxide is dissolved in any acid—for instance, hydrochloric—which does not act as an oxidising agent, a ferrous salt is first formed and ferric oxide remains, which is also capable of passing into solution. The best way of preparing the hydrate of the magnetic oxide is by decomposing a mixture of ferrous and ferric salts with ammonia ; it is, however, indispensable to pour this mixture into the ammonia, and not *vice versa*, as in that case the ferrous oxide would at first be precipitated alone, and then the ferric oxide. The compound thus formed has a bright-green colour, and when dried forms a black powder. Other combinations of ferrous with ferric oxide are known, as also are compounds of ferric oxide

The most simple oxidising agent for transforming ferrous into ferric salts is chlorine in the presence of water—for instance, $2\text{FeCl}_2 + \text{Cl}_2 = \text{Fe}_2\text{Cl}_6$, or generally, $2\text{FeO} + \text{Cl}_2 + \text{H}_2\text{O} = \text{Fe}_2\text{O}_3 + 2\text{HCl}$. When such a transformation is required, it is best to add to the ferrous solution, potassium chlorate and hydrochloric acid; chlorine is formed by their mutual reaction and acts as an oxidising agent. Nitric acid produces a similar effect, although more slowly. Ferrous salts may be completely and rapidly oxidised into ferric salts by means of chromic acid or permanganic acid, HMnO_4 , in the presence of acids—for example, $10\text{FeSO}_4 + 2\text{KMnO}_4 + 8\text{H}_2\text{SO}_4 = 5\text{Fe}_2(\text{SO}_4)_3 + 2\text{MnSO}_4 + \text{K}_2\text{SO}_4 + 8\text{H}_2\text{O}$. This reaction is easily observed by the change of colour, and its termination is easily seen, because potassium permanganate forms solutions of a bright-red colour, and when added to a solution of a ferrous salt the above reaction immediately takes place *in the presence of acid*, and the solution then becomes colourless, because all the substances formed are only faintly coloured in solution. Directly all the ferrous compound has passed into the ferric state, any excess of permanganate which is added communicates a red colour to the liquid (see Chap. XXI.).

Thus, when ferrous salts, FeX_2 , are acted on by oxidising agents, they pass into the ferric form, FeX_3 , whilst under the action of reducing agents the reverse reaction occurs. Sulphuretted hydrogen may, for instance, be used for this complete transformation, for under its influence ferric salts are reduced with separation of sulphur—for example, $\text{Fe}_2\text{Cl}_6 + \text{H}_2\text{S} = 2\text{FeCl}_2 + 2\text{HCl} + \text{S}$. Sodium thiosulphate acts in a similar way: $\text{Fe}_2\text{Cl}_6 + \text{Na}_2\text{S}_2\text{O}_3 + \text{H}_2\text{O} = 2\text{FeCl}_2 + \text{Na}_2\text{SO}_4 + 2\text{HCl} + \text{S}$. Metallic iron or zinc,²⁰ in the presence of acids, or sodium amalgam, &c., acts like hydrogen, and has also a similar reducing action, and this furnishes the best method for reducing ferric salts to ferrous salts—for instance, Fe_2Cl_6

with other bases. Thus, for instance, compounds are known containing 4 molecules of ferrous oxide to 1 of ferric oxide. These are also magnetic, and are formed by heating iron in air. The magnesia compound, $\text{MgO}, \text{Fe}_2\text{O}_3$, is prepared by passing gaseous hydrochloric acid over a heated mixture of magnesia and ferric oxide. Crystalline magnesium oxide is then formed, and black shiny octahedral crystals of the above-mentioned composition. This compound is analogous to the aluminates—for instance, to spinel. Bernheim (1888) and Rousseau (1891) obtained many similar compounds of ferric oxide, and their composition apparently corresponds with that of the hydrates (note 22) known for the oxide.

²⁰ Copper and cuprous salts also reduce ferric oxide to ferrous oxide, and are themselves turned into cupric salts. The essence of the reactions is expressed by the following equations: $\text{Fe}_2\text{O}_3 + \text{Cu}_2\text{O} = 2\text{FeO} + 2\text{CuO}$; $\text{Fe}_2\text{O}_3 + \text{Cu} = 2\text{FeO} + \text{CuO}$. This fact is made use of in analysing copper compounds, the quantity of copper being ascertained by the amount of ferrous salt obtained. An excess of ferric salt is required to complete the reaction. Here we have an example of reverse reaction; the ferrous oxide or its salt in the presence of alkali transforms the cupric oxide into cuprous oxide and metallic copper, as was observed by Lovel, Knopp, and others.

+ Zn = 2FeCl₂ + ZnCl₂. Thus the transition from ferrous salts to ferric salts, or vice versa, is always possible.²¹

Ferric oxide, or sesquioxide of iron, Fe₂O₃, is found in nature, and is artificially prepared in the form of a red powder by many methods. Thus, after heating green vitriol, a red oxide of iron remains, called **colcothar**, which is used as an oil paint, principally for painting wood. The same substance in the form of a very fine powder (*rouge*) is used for polishing glass, steel, and other objects. If a mixture of ferrous sulphate with an excess of common salt be strongly heated, crystalline ferric oxide will be formed, having a dark-violet colour, and resembling certain natural varieties of this substance. When iron pyrites is heated for preparing sulphurous anhydride, ferric oxide also remains behind; it is used as a pigment. On the addition of an alkali to a solution of a ferric salt, a brown precipitate of ferric hydroxide is formed, which when heated (even when boiled in water, that is, at about 100°, according to Tomassi) easily parts with the water, and leaves red anhydrous ferric oxide. Pure ferric oxide does not show any magnetic properties, but when heated to a white heat it loses oxygen and is converted into the magnetic oxide. Anhydrous ferric oxide which has been heated to a high temperature is with difficulty soluble in acids (but it is soluble when heated in strong acids, and also when fused with potassium hydrogen sulphate), whilst ferric hydroxide, at all events that which is precipitated from salts by means of alkalies, is very readily soluble in acids. The precipitated **ferric hydroxide** has the composition 2Fe₂O₃, 3H₂O, or Fe₄H₆O₉. If this ordinary hydroxide is rendered anhydrous (by heating), at a certain moment it becomes incandescent—that is, it loses a certain quantity of heat. This self-incandescence depends on internal displacement produced by the transition of the easily soluble (in acids) variety into the difficultly soluble variety, and does not

²¹ We shall here mention the reactions by means of which it may be ascertained whether the ferrous compound has been entirely converted into a ferric compound, or *vice versa*. There are two substances which are best employed for this purpose: potassium ferrieyanide, FeK₃C₆N₆, and potassium thiocyanate, KCNS. The first of these gives with ferrous salts a blue precipitate of an insoluble salt, having a composition Fe₅C₁₂N₁₂; but with ferric salts it does not form any precipitate, and only gives a brown colour, and therefore when transforming a ferrous salt into a ferric salt, the completion of the transformation may be detected by taking a drop of the liquid on paper or on a porcelain plate and adding a drop of the ferrieyanide solution. If a blue precipitate is formed, part of the ferrous salt still remains; if there is none, the transformation is complete. The thiocyanate does not give any marked coloration with ferrous salts; but with ferric salts in the most dilute state it forms a bright-red soluble compound, and therefore, when transforming a ferric salt into a ferrous salt, we must proceed as before, testing a drop of the solution with thiocyanate, when the absence of a red colour will prove the total transformation of the ferric salt into the ferrous state, and if a red colour appears it shows that the transformation is not yet complete.

depend on the loss of water, since the anhydrous oxide undergoes the same change. In addition to this there exists a ferric hydroxide, or hydrated oxide of iron, which, like the strongly heated anhydrous iron oxide, is difficultly soluble in acids. On losing water, or after the loss of water, this hydroxide does not undergo such self-incandescence, because no such internal displacement (loss of energy or heat) occurs with it as that which is peculiar to the ordinary oxide of iron. The ferric hydroxide which is difficultly soluble in acids has the composition $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$. This hydroxide is obtained by prolonged ebullition of water in which ferric hydroxide, prepared by the oxidation of ferrous oxide, is suspended, and also sometimes by similar treatment of the ordinary hydroxide, after it has been for a long time in contact with water. The transition of one hydroxide to another is apparent by a change of colour; the easily soluble hydroxide is redder, and the sparingly soluble hydroxide more yellow in colour.²²

The normal salts of the composition Fe_2X_6 or FeX_3 correspond with ferric oxide—for example, the exceedingly volatile **ferric chloride**, Fe_2Cl_6 , which is easily prepared in the anhydrous state by the action of chlorine on heated iron.²³ Such also is the normal **ferric nitrate**,

²² The **two ferric hydroxides** are characterised not only by the above-mentioned properties, but also by the fact that with potassium ferrocyanide, $\text{K}_4\text{FeC}_6\text{N}_6$, the first hydroxide immediately gives a blue colour depending on the formation of Prussian blue, whilst the second hydroxide does not give any reaction whatever with this salt. The first hydroxide is entirely soluble in nitric, hydrochloric, and all other acids; whilst the second sometimes (not always) forms a brick-coloured liquid, which appears turbid and does not give the reactions peculiar to the ferric salts (Péan de Saint-Gilles, Scheurer-Kestner). In addition to this, when the smallest quantity of an alkaline salt is added to this liquid, ferric oxide is precipitated. Thus, a colloidal solution is formed (hydrosol), which is exactly similar to the hydrosol of silica (Chap. XVII.), according to which example the hydrosol of ferric oxide may be obtained.

If ordinary ferric hydroxide is dissolved in acetic acid, a solution of the colour of red wine is obtained, which has all the reactions characteristic of ferric salts. But if this solution (formed in the cold) is heated to the boiling-point, its colour is very rapidly intensified, a smell of acetic acid becomes apparent, and the solution then contains a new variety of ferric oxide. If the boiling of the solution is continued, acetic acid is evolved, and the modified ferric oxide is precipitated. If the evaporation of the acetic acid is prevented (in a closed or sealed vessel), and the liquid heated for some time, the whole of the ferric hydroxide passes into the insoluble form, and if some alkaline salt be added (to the hydrosol formed), the whole of the ferric oxide will then be precipitated in its insoluble form.

All the phenomena observed respecting ferric oxide (colloidal properties, various forms, formation of double basic salts) demonstrate that this substance, like silica, alumina, Cr_2O_3 , lead hydroxide, &c., is polymerised, and that the composition is represented by $(\text{Fe}_2\text{O}_3)_n$.

²³ The ferric compound which is most used in practice (for instance, in medicine, for cauterising, stopping bleeding, &c.—Oleum Martis) is **ferric chloride**, Fe_2Cl_6 , easily obtainable by dissolving the ordinary hydrated oxide of iron in hydrochloric acid. It is obtained in the anhydrous state by the action of chlorine on heated iron. The experiment is carried on in a porcelain tube, and a solid **volatile substance** is then formed in

$\text{Fe}_2(\text{NO}_3)_6$; it is obtained by dissolving iron in an excess of nitric acid, the shape of brilliant violet scales which very readily absorb moisture from the air, and when heated with water decompose into crystalline ferric oxide and hydrochloric acid: $\text{Fe}_2\text{Cl}_6 + 3\text{H}_2\text{O} = 6\text{HCl} + \text{Fe}_2\text{O}_3$. Ferric chloride is so volatile that the density of its vapour may be determined. At 440° this has the value 164.0 referred to hydrogen; the formula Fe_2Cl_6 corresponds with a density of 162.5. An aqueous solution of this salt has a brown colour. On evaporating and cooling the solution, crystals separate containing 6 or 12 molecules of H_2O , so that the solution then probably contains, not Fe_2Cl_6 , but $\text{Fe}_2(\text{OH})_6, 6\text{HCl}$, although this cannot be stated with certainty. Ferric chloride is soluble not only in water, but also in alcohol (similarly to magnesium chloride, &c.) and in ether. If the latter solutions are exposed to the rays of the sun, they become colourless, and deposit ferrous chloride, FeCl_2 , chlorine being disengaged. After a certain lapse of time, the aqueous solutions of ferric chloride decompose with precipitation of a basic salt, thus demonstrating the instability of ferric chloride, like the other salts of ferric oxide (note 22). This salt is much more stable in the form of double salts, like all the ferric salts, and also the salts of many other feeble bases. Potassium (or ammonium) chloride forms with it very beautiful red crystals of a double salt, having the composition

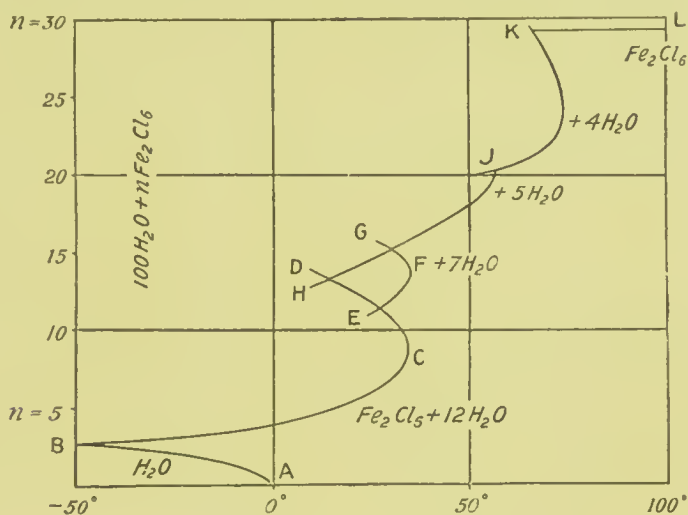


FIG. 106.—Diagram of the solubility of Fe_2Cl_6 .

$\text{Fe}_2\text{Cl}_6, 4\text{KCl}, 2\text{H}_2\text{O}$. When a solution of this salt is evaporated it decomposes, with separation of potassium chloride.

B. Roozeboom (1892) studied in detail (as for CaCl_2 , Chap. XIV., note 50) the separation of different hydrates from saturated solutions of Fe_2Cl_6 at various concentrations and temperatures; he found that there are 4 crystallohydrates, with 12, 7, 5, and 4 molecules of water respectively. An orange-yellow only slightly hygroscopic hydrate, $\text{Fe}_2\text{Cl}_6, 12\text{H}_2\text{O}$, is most easily and usually obtained and melts at 37° ; its solubility at different temperatures is represented by the curve BCD in the accompanying figure, where the point B corresponds to the formation, at -55° , of a cryohydrate containing about $\text{Fe}_2\text{Cl}_6 + 36\text{H}_2\text{O}$, the point C to the melting-point ($+37^\circ$) of the hydrate $\text{Fe}_2\text{Cl}_6, 12\text{H}_2\text{O}$, and the curve CD to the fall in the temperature of crystallisation with an increase in the amount of salt or a decrease in the amount of water (in the figure the temperatures are taken along the axis of abscissæ, and the magnitude of n in the formula $n\text{Fe}_2\text{Cl}_6 + 100\text{H}_2\text{O}$ along the axis of ordinates). When anhydrous Fe_2Cl_6 is added to the above hydrate ($12\text{H}_2\text{O}$), or some of the water is evaporated from the latter, very hygroscopic crystals of $\text{Fe}_2\text{Cl}_6, 5\text{H}_2\text{O}$ (Fritzsche) are formed; they melt at 56° , and their solubility is expressed by the curve HJ, which also presents a small branch at the end J. This again gives the fall in the temperature of crystallisation with an increase

taking care as far as possible to prevent any rise of temperature.²⁴ The normal salt separates from the brown solution when it is concentrated

in the amount of Fe_2Cl_6 . Besides these curves and the solubility of the anhydrous salt expressed by the line KL (up to 100° , beyond which chlorine is liberated), Roozeboom also gives the two curves, EFG and JK, corresponding to the crystalline hydrates, $\text{Fe}_2\text{Cl}_6 \cdot 7\text{H}_2\text{O}$ (melts at $+32.5^\circ$, that is, lower than any of the others) and $\text{Fe}_2\text{Cl}_6 \cdot 4\text{H}_2\text{O}$ (melts at 73.5°), which he discovered by a systematic research on the solutions of ferric chloride.

The researches of the same Dutch chemist upon the conditions of the formation of crystals from the double salt $(\text{NH}_4\text{Cl})_4 \cdot \text{Fe}_2\text{Cl}_6 \cdot 2\text{H}_2\text{O}$ are even more complete. This salt was obtained in 1839 by Fritzsche, and is easily formed from a strong solution of Fe_2Cl_6 by adding sal-ammoniac, when it separates in crimson rhombic crystals, which, after dissolving in water, only deposit again on evaporation, together with the sal-ammoniac.

Roozeboom (1892) found that when the solution contains b molecules of Fe_2Cl_6 and a molecules of NH_4Cl , per 100 molecules of H_2O , then at 15° one of the following separations takes place: (1) crystals, $\text{Fe}_2\text{Cl}_6 \cdot 12\text{H}_2\text{O}$, when a varies between 0 and 1.1 and b between 4.65 and 4.8, or (2) a mixture of these crystals and the double salt, when a is 1.36, and b , 4.47, or (3) the double salt, $\text{Fe}_2\text{Cl}_6 \cdot 4\text{NH}_4\text{Cl} \cdot 2\text{H}_2\text{O}$, when a varies between 2 and 11.8, and b between 3.1 and 4.65, or (4) a mixture of sal-ammoniac with the iron salt (it crystallises in separate cubes, Retgers, Lehmann), when a varies between 7.7 and 10.9, and b is less than 3.38, or (5) sal-ammoniac, when a is 11.88. And as in the double salt, $a : b :: 4 : 1$, it is evident that the double salt only separates out when the ratio $a : b$ is less than 4 : 1 (i.e., when Fe_2Cl_6 predominates). The above is seen more clearly in the



FIG. 107.—Diagram of the formation, at 15° , of the double salt $\text{Fe}_2\text{Cl}_6 \cdot 4\text{NH}_4\text{Cl} \cdot 2\text{H}_2\text{O}$ or $\text{Fe}(\text{NH}_4)_2\text{Cl}_5 \cdot \text{H}_2\text{O}$. (After Roozeboom.)

accompanying figure, where a , or the number of molecules of NH_4Cl per 100 H_2O , is taken along the axis of abscissæ, and b , or the number of molecules of Fe_2Cl_6 , along the ordinates. The curves ABCD correspond to saturation, and present the isotherm of 15° . The portion AB corresponds to the separation of Fe_2Cl_6 (the ascending nature of this curve shows that the solubility of Fe_2Cl_6 is increased by the presence of NH_4Cl , while that of NH_4Cl decreases in the presence of Fe_2Cl_6), the portion BC to the double salt, and the portion CD to a mixture of sal-ammoniac and ferric chloride, while the straight line OF corresponds to the ratio $\text{Fe}_2\text{Cl}_6 \cdot 4\text{NH}_4\text{Cl}$, or $a : b :: 4 : 1$. The portion CE shows that more double salt may be introduced into the solution without decomposition, but then the solution deposits a mixture of sal-ammoniac and ferric chloride (see Chap. XXIV., note 9a). If there were more such well-investigated cases of solutions, our knowledge of double salts, solutions, the influence of water, equilibria, isomorphous mixtures, and suchlike provinces of chemical relations might be considerably advanced. The subject belongs to the province of physical chemistry.

²⁴ The normal ferric salts are decomposed by heat and even by water, forming basic salts, which may be prepared in various ways. Normal ferric hydroxide is dissolved in solutions of ferric nitrate; if these contain a double quantity of iron the basic salt is formed which contains Fe_2O_3 (in the form of hydroxide) $+ 2\text{Fe}_2(\text{NO}_3)_6 = 3\text{Fe}_2\text{O}(\text{NO}_3)_4$,

under a bell-jar over sulphuric acid. This salt, $\text{Fe}_2(\text{NO}_3)_6 \cdot 9\text{H}_2\text{O}$, then crystallises in well-formed and perfectly colourless crystals,²⁵ which deliquesce in the air, melt at 35° , and are soluble in and decomposed by water. The decomposition may be seen from the fact that the solution is brown and does not yield the whole of the salt again, but gives

a salt of the type Fe_2OX_4 . Probably water enters into its composition. With considerable quantities of ferric oxide, insoluble basic salts are obtained containing various amounts of ferric hydroxide. Thus, when a solution of the above-mentioned basic acid is boiled, a precipitate is formed containing $4(\text{Fe}_2\text{O}_3)_3 \cdot 2(\text{N}_2\text{O}_5) \cdot 3\text{H}_2\text{O}$, which probably contains $2\text{Fe}_2\text{O}_2(\text{NO}_3)_2 + 2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$. If a solution of basic nitrate is sealed in a tube and then immersed in boiling water, the colour of the solution changes just in the same way as if a solution of ferric acetate had been employed (note 22) and in the same manner as the salts of Cr_2O_3 . The solution obtained smells strongly of nitric acid, and on adding a drop of sulphuric or hydrochloric acid the insoluble variety of hydrated ferric oxide is precipitated.

Normal ferric orthophosphate is soluble in sulphuric, hydrochloric, and nitric acids, but insoluble in others, such as, for instance, acetic acid. The composition of this salt in the anhydrous state is FePO_4 , because in orthophosphoric acid there are three atoms of hydrogen, and iron, in the ferric state, replaces these three atoms. This salt is obtained from ferric acetate, which, with disodium phosphate, forms a *white precipitate* of FePO_4 , containing water. If a solution of ferric chloride (yellowish-red colour) be mixed with a solution of sodium acetate in excess, the liquid assumes an intense brown colour, which demonstrates the formation of a certain quantity of ferric acetate; the disodium phosphate also forms a white gelatinous precipitate of ferric phosphate. By this means the whole of the iron may be precipitated, and the liquid, which was brown, then becomes colourless. If this normal salt be dissolved in orthophosphoric acid, the crystalline acid salt, $\text{FeH}_3(\text{PO}_4)_2$, is formed. If there be an excess of ferric oxide in the solution, the precipitate will consist of the basic salt. If ferric phosphate is dissolved in hydrochloric acid and ammonia added, on heating, a salt is precipitated which, after continued washing in water and heating (to remove the water), has the composition $\text{Fe}_4\text{P}_2\text{O}_{11}$ —that is, $2\text{Fe}_2\text{O}_3 \cdot \text{P}_2\text{O}_5$. In an aqueous condition this salt may be considered as ferric hydroxide, $\text{Fe}_2(\text{OH})_6$, in which $(\text{OH})_3$ is replaced by the equivalent group PO_4 . Whenever ammonia is added to a solution containing an excess of a ferric salt and a certain amount of phosphoric acid, a precipitate is formed containing the whole of the phosphoric acid in the mass of the ferric oxide.

Ferric oxide is characterised as a feeble base, and also by the fact of its forming double salts—for instance, **potassium iron alum**, which has a composition $\text{Fe}_2(\text{SO}_4)_3 \cdot \text{K}_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$, or $\text{FeK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$. It is obtained in the form of almost colourless or light rose-coloured large octahedra of the regular system by simply mixing solutions of potassium sulphate and the ferric sulphate obtained by dissolving ferric oxide in sulphuric acid. The rubidium iron alums readily crystallise at $+2^\circ$, $+3^\circ$, but melt and decompose at 33° (Erdmann). This may be taken advantage of for separating Rb from K.

²⁵ It would seem that all normal hydrated ferric salts are colourless, and that the brown colour peculiar to their solutions is really due to basic ferric salts. A remarkable example of the apparent change of colour of salts is represented by the ferrous and ferric oxalates. The former in a dry state has a yellow colour, although, as a rule, the ferrous salts are green, and the latter is colourless or pale green. When the normal ferric salt is dissolved in water it is, like many salts, probably decomposed by the water into acid and basic salts, and the latter communicates a brown colour to the solution. Iron alum is almost colourless, is easily decomposed by water, and is the best proof of the above assertion. A parallel study of the phenomena peculiar to ferric and chromic salts might, in my opinion, give a very useful addition to our knowledge of the aqueous solutions of salts in general.

partly basic salt. The normal salt (only stable in the presence of an excess of HNO_3) is completely decomposed with great facility by heating, even with water, at 130° , and this is made use of for removing iron (and also certain other oxides of the form R_2O_3) from many other bases (of the form RO) whose nitrates are far more stable. The ferric salts, FeX_3 , in passing into ferrous salts, act as oxidising agents, as is seen from the fact that they liberate not only S from SH_2 , but also iodine from KI , like many oxidising agents.^{25a}

Iron forms one other oxide besides the ferric and ferrous oxides; this contains twice as much oxygen as the former, but is so very unstable that it can be obtained neither in the free state nor as a hydrate. Whenever such conditions of double decomposition occur as should allow of its separation in the free state, it decomposes into oxygen and ferric oxide. It is known in the form of salts, and is only stable in the presence of alkalies, with which it gives salts having a decidedly alkaline reaction; it is therefore a feebly acid oxide. When small pieces of iron are heated with nitre or potassium chlorate, a potassium salt of the composition K_2FeO_4 is formed. The same salt is formed when cast iron (but not pure iron) is used as an anode in a solution of potash. The hydrate corresponding with this salt should have the composition H_2FeO_4 . It is called **ferric acid**. Its anhydride ought to contain FeO_3 or Fe_2O_6 —twice as much oxygen as ferric oxide. If a solution of potassium ferrate be mixed with acid, the free hydrate ought to be formed, but it immediately decomposes ($2\text{K}_2\text{FeO}_4 + 5\text{H}_2\text{SO}_4 = 2\text{K}_2\text{SO}_4 + \text{Fe}_2(\text{SO}_4)_3 + 5\text{H}_2\text{O} + \text{O}_3$), oxygen being

^{25a} The reaction $\text{FeX}_3 + \text{KI} = \text{FeX}_2 + \text{KX} + \text{I}$ proceeds comparatively slowly in solutions, is not complete (depends upon the mass), and is reversible. In this connection we may cite the following data from Seubert and Rohrer's (1894) comprehensive researches. The investigations were conducted with solutions containing $\frac{1}{10}$ gram-equivalent weights of $\text{Fe}_2(\text{SO}_4)_3$ (i.e., containing 20 grams of salt per litre), and a corresponding solution of KI , the amount of iodine liberated being determined (after the addition of starch) by a solution (also $\frac{1}{10}$ normal) of $\text{Na}_2\text{S}_2\text{O}_3$ (see Chap. XX., note 42). The progress of the reaction was expressed by the amount of iodine liberated in percentages of the theoretical amount. For instance, the following amount of iodide of potassium was decomposed when $\text{Fe}_2(\text{SO}_4)_3 + 2n\text{KI}$ was taken:

$n =$	1	2	3	6	10	20
After 15'	11.4	26.3	40.6	73.5	91.6	96.0
" 30'	14.0	35.8	47.8	78.5	94.3	97.4
" 1 hour	19.0	42.7	56.0	84.0	95.7	97.6
" 10 hours	32.6	56.0	75.7	93.2	96.5	97.6
" 48 "	39.4	67.7	82.6	93.4	96.6	97.6

Similar results were obtained for FeCl_3 , but there the amount of iodine liberated was somewhat greater. Similar results were also obtained by increasing the mass of FeX_3 relatively to that of the KI , and by replacing it by HI (see Chap. XXI., note 26). Such instances as these show that the rate of chemical reaction and the influence of the reacting masses are questions of special interest to modern theoretical chemistry.

evolved. If a small quantity of acid is taken, or if a solution of potassium ferrate is heated with solutions of other metallic salts, ferric oxide is separated—for instance :



Both these oxides are of course deposited in the form of hydrates. This shows that not only the hydrate H_2FeO_4 , but also the salts of the heavy metals corresponding with this higher oxide of iron, are not formed by reactions of double decomposition. But the barium salt, which is only slightly soluble in water, is formed by adding BaCl_2 , which points to a certain resemblance to sulphuric acid. The solution of potassium ferrate naturally acts as a powerful oxidising agent; for instance, it transforms manganous oxide into the dioxide, sulphurous into sulphuric acid, oxalic acid into carbonic anhydride and water, &c.²⁶

Iron thus combines with oxygen in three proportions: RO , R_2O_3 , and RO_3 . It might have been expected that there would be intermediate stages, RO_2 (corresponding to pyrites, FeS_2) and R_2O_5 , but for iron these are unknown.^{26a} The lower oxide has a distinctly basic character, the higher is feebly acid. The only one which is stable in the free state is ferric oxide, Fe_2O_3 ; the suboxide, FeO , absorbs oxygen, and ferric anhydride, FeO_3 , evolves it. It is also the same with other elements; the character of each is determined by the relative

²⁶ If chlorine is passed through a strong solution of potassium hydroxide in which hydrated ferric oxide is suspended, the turbid liquid acquires a dark pomegranate-red colour and contains potassium ferrate: $10\text{KHO} + \text{Fe}_2\text{O}_3 + 3\text{Cl}_2 = 2\text{K}_2\text{FeO}_4 + 6\text{KCl} + 5\text{H}_2\text{O}$. The chlorine must not be in excess, otherwise the salt is again decomposed, although the mode of decomposition is unknown; probably ferric chloride and potassium chlorate are formed.

^{26a} After Mond and his assistants obtained the remarkable volatile compound $\text{Ni}(\text{CO})_4$ (described later), it was shown by Mond and Quincke (1891), and also by Berthelot, that iron, under certain conditions, in a stream of carbonic oxide, also volatilises and forms a compound like that given by nickel. Roscoe and Scudder then showed that when water gas is passed through and kept under pressure (8 atmospheres) in iron vessels a portion of the iron volatilises from the sides of the vessel, and that when the gas is burnt it deposits a certain amount of oxides of iron (the same result is obtained with ordinary coal gas, which contains a small amount of CO). To obtain the volatile compound of iron with carbonic oxide, Mond prepared a finely divided iron by heating the oxalate in a stream of hydrogen, and after cooling this to $80^\circ - 45^\circ$, passed CO over it. The iron then formed (although very slowly) a volatile compound of the composition $\text{Fe}(\text{CO})_5$ (as though it answered to a very high type, FeX_{10}), which when cooled condenses into a liquid (slightly coloured, probably owing to incipient decomposition), of sp. gr. 1.47, which solidifies at -21° , boils at about 103° , and has a vapour density (about 6.5 with respect to air) corresponding with the above formula; it decomposes at 180° . Water and dilute acids do not act upon it, but it decomposes under the action of light and forms a hard, non-volatile crystalline yellow compound, $\text{Fe}_2(\text{CO})_7$, which decomposes at 80° and again forms $\text{Fe}(\text{CO})_5$.

degree of stability of the known oxides. The salts FeX , correspond with the suboxide, the salts FeX_3 or Fe_2X_6 with the sesquioxide, and FeX_6 represents those of ferric acid, as its potassium salt is $\text{FeO}_2(\text{OK})_2$, corresponding with K_2SO_4 , K_2MnO_4 , K_2CrO_4 , &c. Iron therefore forms compounds of the types FeX_2 , FeX_3 , and FeX_6 , but this latter, like the type NX_5 , does not appear separately, but only when X represents heterogeneous elements or groups; for instance, for nitrogen in the form of $\text{NO}_2(\text{OH})$, NH_4Cl , &c., for iron in the form of $\text{FeO}_2(\text{OK})_2$. But still the type FeX_6 exists, and therefore FeX_2 and FeX_3 are compounds which, like ammonia, NH_3 , are capable of further combinations up to FeX_6 ; this is perhaps also partly seen in the property of ferrous and ferric salts of forming compounds with water of crystallisation, besides double and basic salts, the stability of which is determined by the quality of the elements included in the types FeX_2 and FeX_3 . It is therefore to be expected that there should be complex compounds derived from ferrous and ferric oxides. Amongst these the series of cyanogen compounds is particularly interesting; their formation and character are determined not only by the property which iron possesses of forming complex types, but also by the similar faculty of the cyanogen compounds, which, like nitriles (Chap. IX.), have clearly developed properties of polymerisation and in general of forming complex compounds.²⁷

In the cyanogen compounds of iron, two degrees might be expected: $\text{Fe}(\text{CN})_2$, corresponding with ferrous oxide, and $\text{Fe}(\text{CN})_3$, corresponding with ferric oxide. There are actually, however, many other known compounds, intermediate and far more complex. They correspond with the double salts so easily formed by metallic cyanides. The two following double salts are particularly well known, very stable, often used, and easily prepared. **Potassium ferrocyanide or yellow prussiate of potash**, a double salt of cyanide of potassium and ferrous cyanide, has the composition $\text{FeC}_2\text{N}_2, 4\text{KCN}$; its crystals contain 3 mols. of water: $\text{K}_4\text{FeC}_6\text{N}_6, 3\text{H}_2\text{O}$. The other is **potassium ferricyanide or red prussiate of potash**. It is also known as **Gmelin's salt**, and contains cyanide of potassium with ferric cyanide; its composition is $\text{Fe}(\text{CN})_3, 3\text{KCN}$ or $\text{K}_3\text{FeC}_6\text{N}_6$. Its crystals do not contain water. It is obtained from

²⁷ Some light may be thrown upon the faculty of Fe of forming various compounds with CN, by the fact that Fe not only combines with carbon but also with nitrogen. *Nitride of iron*, Fe_2N , was obtained by Fowler by heating finely powdered iron in a stream of NH_3 at the temperature of melting lead, but this experiment has not been verified. Judging from their reactions, the ferrieyanides belong to the class of 'complex' compounds which present some analogy to the organic compounds, for the Fe and CN in the ferrieyanides do not react in the usual manner, like the acid elements in organic compounds.

the first by the action of chlorine, which removes one atom of the potassium. A whole series of other **ferrocyanic compounds** correspond with these ordinary salts. Before treating of the preparation and properties of these two remarkable and very stable salts, it must be observed that with ordinary reagents neither of them gives the same double decompositions as the other ferrous and ferric salts, and they both present a series of remarkable and original reactions.^{27a} Thus solutions of these salts have a neutral reaction (that of KCN is alkaline) and are unchanged by air, dilute acids, or water (unlike potassium cyanide). Caustic alkalies do not give a precipitate of ferrous or ferric hydroxide from solutions of these salts, which are also not precipitated by sodium carbonate. This led the earlier investigators to recognise special independent groupings in them. The yellow prussiate was considered to contain the complex radicle FeC_6N_6 combined with potassium, namely, with K_4 , while in the red prussiate the same complex is combined with K_3 . This was confirmed by the fact that whilst in both salts any other metal, even hydrogen, might be substituted for potassium, the iron remained unchangeable, just as the nitrogen in cyanogen, ammonium, and nitrates does not enter into double decomposition, being in the state of the complex radicles, CN , NH_4 , NO_2 . Such a representation is, however, quite superfluous for the explanation of the peculiarities in the reactions of such compounds as double salts. If a magnesium salt which can be precipitated by potassium hydroxide does not form a precipitate in the presence of ammonium chloride, it is very clear that it is owing to the formation of a soluble double salt which is not decomposed by alkalies. And there is no necessity to account for the peculiarity of reaction of a double salt by the formation of a new complex radicle. In the same way also, in the presence of an excess of tartaric acid, cupric salts do not form a precipitate with potassium hydroxide, because a double salt is formed. These peculiarities are more easily

^{27a} Which is, indeed, the property of the so-called 'complex' compounds, concerning which I have already given, and shall subsequently give my opinion. I think the recognition of complex radicles or residues is mostly and generally a simple statement or expression of a fact, and helps very little towards gaining a deeper insight into the properties of chemical compounds, &c., which ought to be the chief aim of all perfect knowledge. For example, the recognition of $\text{Fe}(\text{CN})_6$ does not show that this residue combines with K_3 and K_4 ; it does not exist in a free state, does not form $\text{R}(\text{OH})_n$ or $\text{R}(\text{NH}_2)_n$, &c., and those qualities proper to its compounds are most simply and advantageously understood by simply recognising the existence of double salts of ferrous and ferric oxides, and by recognising that, in general, complex molecules composed of polyatomic atoms readily build themselves up in various ways (isomerise) as is seen both in the 'complex' and in carbon compounds. A comprehension of the structure and mode of building up will require as complete a study of the reactions as exists for the organic compounds. These considerations incline me to the opinion that the recognition of a radicle, $\text{Fe}(\text{CN})_6$, is unnecessary.

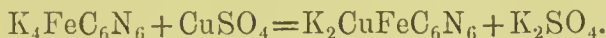
understood in the case of cyanogen compounds than in all others, because all cyanogen compounds, as unsaturated compounds, show a marked tendency to complexity. This tendency is satisfied in double salts. The appearance of a peculiar character in double cyanides is the more easily understood, since in the case of potassium cyanide itself, and also in hydrocyanic acid, a great many peculiarities have been observed which are not encountered in those haloid compounds, potassium chloride and hydrochloric acid, with which it was *usual* to compare cyanogen compounds. These peculiarities become more comprehensible on comparing cyanogen compounds with ammonia compounds. Thus in the presence of ammonia the reactions of many compounds change considerably. If in addition to this it is remembered that the presence of many carbon (organic) compounds frequently completely disturbs the reactions of salts, the peculiarities of certain double cyanides will appear still less strange, because they contain carbon. The fact that the presence of carbon or another element in the compound produces a change in the reactions may be compared with the action of oxygen, which, when entering into a combination, also very materially changes the nature of reactions. Chlorine is not detected by silver nitrate when it is in the form of potassium chlorate, KClO_3 , as it is detected in potassium chloride, KCl . The iron in ferrous and ferric compounds varies in its reactions. In addition to the above-mentioned facts, consideration ought to be given to the circumstance that the easy mutability of nitric acid undergoes modification in its alkali salts, and in general the properties of a salt often differ much from those of the acid. Every double salt ought to be regarded as a peculiar kind of saline compound : potassium cyanide is, as it were, a basic, and ferrous cyanide an acid, element. They may be more or less unstable in the separate state, but form a stable double compound when combined together ; the act of combination disengages the energy of the elements, and they, so to speak, saturate each other. Of course, all this is not a definite explanation, but then the supposition of a special complex radicle can even less be regarded as such.

Potassium ferrocyanide, $\text{K}_4\text{FeC}_6\text{N}_6$, is very easily formed by mixing solutions of ferrous sulphate and potassium cyanide. First, a white precipitate of ferrous cyanide, FeC_2N_2 , is formed, which becomes blue on exposure to air, but is soluble in an excess of potassium cyanide, forming the ferrocyanide. The same yellow prussiate is obtained on heating nitrogenous animal charcoal or animal matters—such as horn, leather cuttings, &c.—with potassium carbonate in iron vessels,^{27b}

^{27b} The sulphur of the animal refuse here forms the compound FeKS_2 , which, by the action of potassium cyanide, yields potassium sulphide, thiocyanate, and ferrocyanide.

the mass formed being afterwards boiled with water with exposure to air, potassium cyanide first appearing, which gives yellow prussiate. The animal charcoal may be exchanged for wood charcoal, permeated with potassium carbonate and heated in nitrogen or ammonia; the mass thus produced is then boiled in water with ferric oxide.²⁸ In this manner it is manufactured on the large scale, and is called **yellow prussiate** (*prussiate de potasse*, *Blutlaugensalz*).

It is easy to substitute other metals for the potassium in the yellow prussiate by double decomposition. The hydrogen salt or **hydroferrocyanic acid**, $\text{H}_4\text{FeC}_6\text{N}_6$, is obtained by mixing strong solutions of yellow prussiate and hydrochloric acid. If ether is added and the air excluded, the acid is obtained directly in the form of a white scarcely crystalline precipitate which becomes blue on exposure to air (as ferrous cyanide does from the formation of blue compounds of ferrous and ferric cyanides, on which account it is used in cotton printing). It is soluble in water and alcohol, but not in ether, has marked acid properties, and decomposes carbonates, thus rendering it easily possible to prepare ferrocyanides of the metals of the alkalis and alkaline earths; these are readily soluble, have a neutral reaction, and resemble the yellow prussiate. Solutions of these salts form precipitates with the salts of other metals, because the ferrocyanides of the heavy metals are insoluble. Either the whole of the potassium, K_4 , of the yellow prussiate, or only a part of it, is exchanged for an equivalent quantity of the heavy metal. Thus, when a cupric salt is added to a solution of yellow prussiate, a red precipitate is obtained which still contains half the potassium of the yellow prussiate:



But if the process be reversed (the salt of copper being then in excess), the whole of the potassium will be exchanged for copper, forming a reddish-brown precipitate, $\text{Cu}_2\text{FeC}_6\text{N}_6 \cdot 9\text{H}_2\text{O}$. This reaction and those similar to it^{28a} are very sensitive, and may be used for detecting

²⁸ Potassium ferrocyanide may also be obtained from Prussian blue by boiling with a solution of potassium hydroxide, and from the ferricyanide by the action of alkalis and reducing substances (because the red prussiate is a ferric salt, and is reduced to a ferrous salt), &c. In many works (especially in Germany and France) yellow prussiate is prepared from the mass, containing oxide of iron, employed for purifying coal gas (Vol. I.), which generally contains cyanogen compounds. About 2 per cent. of the nitrogen contained in coal is converted into cyanogen, which forms Prussian blue and thiocyanates in the mass used for purifying the gas. On evaporation, the solution yields large yellow crystals containing 3 molecules of water, which is easily expelled by heating above 100°. A hundred parts of water at the ordinary temperature are capable of dissolving 25 parts of this salt; its sp. gr. is 1.83. When ignited it forms potassium cyanide and iron carbide, FeC_2 (Chap. XIII., note 12). Oxidising substances change it into potassium ferricyanide. With strong sulphuric acid it gives carbonic oxide, and with dilute sulphuric acid, when heated, prussic acid is evolved.

^{28a} In the interaction of ZnSO_4 and yellow prussiate, Miller and Danziger (1902)

metals in solution, more especially as the colour of the precipitate very often shows a marked variation when one metal is exchanged for another. Zinc, cadmium, lead, antimony, tin, silver, cuprous and aurous salts form **white precipitates**; cupric, uranium, titanium, and molybdenum salts, **reddish-brown**; those of nickel, cobalt, and chromium, **green precipitates**; **with ferrous salts**, ferrocyanide forms, as has been already mentioned, a **white precipitate**—namely, $\text{Fe}_2\text{FeC}_6\text{N}_6$, or FeC_2N_2 —which turns blue on exposure to air, and with ferric salts a **blue precipitate** called **Prussian blue**. Here the potassium is replaced by iron, the reaction being expressed thus: $2\text{Fe}_2\text{Cl}_6 + 3\text{K}_4\text{FeC}_6\text{N}_6 = 12\text{KCl} + \text{Fe}_4\text{Fe}_3\text{C}_{18}\text{N}_{18}$, the latter formula expressing the composition of Prussian blue. It is therefore the compound $4\text{Fe}(\text{CN})_3 + 3\text{Fe}(\text{CN})_2$. The yellow prussiate is prepared in chemical works on a large scale, especially for the manufacture of this blue pigment, which is used for dyeing cloth and other fabrics and also as one of the ordinary blue paints. It is insoluble in water, and the stuffs are therefore dyed by soaking them first in a solution of a ferric salt and then in a solution of yellow prussiate. If, however, an excess of yellow prussiate be present, complete substitution between potassium and iron does not occur, and soluble Prussian blue is formed, $\text{KFe}_2(\text{CN})_6 = \text{KCN}, \text{Fe}(\text{CN})_2, \text{Fe}(\text{CN})_3$. This blue salt is colloidal and soluble in pure water, and is precipitated when other salts—for instance, potassium or sodium chloride—are present even in small quantities, and is therefore first obtained as a precipitate.²⁹

Potassium ferricyanide, or **red prussiate** of potash, $\text{K}_3\text{FeC}_6\text{N}_6$, is

obtained precipitates containing different amounts of Fe, K, and Zn, according as one or the other original salt was in excess, or according to whether acids, ammonia, &c., were present. With excess of the zinc salt and after washing with a solution of ammonia, $\text{Zn}_2\text{Fe}(\text{CN})_6$ was obtained, and with an excess of the yellow prussiate a salt which in the limit had the composition $\text{K}_2\text{Zn}_3\text{Fe}_2(\text{CN})_{12}$.

²⁹ Skraup obtained this salt both from potassium ferrocyanide with ferric chloride and from ferricyanide with ferrous chloride, which evidently shows that it contains iron in both the ferric and ferrous states. With ferrous chloride it forms Prussian blue, and with ferric chloride Turnbull's blue.

Prussian blue was discovered in the beginning of the eighteenth century by Diesbach. Prussian blue has not a crystalline structure; it forms a blue mass with a copper-red metallic lustre. Both acids and alkalies act on it. The action is at first confined to the ferric salt it contains. Thus, alkalies form ferric oxide and ferrocyanide in solution: $2\text{Fe}_2\text{C}_6\text{N}_6 + 3\text{FeC}_2\text{N}_2 + 12\text{KHO} = 2(\text{Fe}_2\text{O}_3, 3\text{H}_2\text{O}) + 3\text{K}_4\text{FeC}_6\text{N}_6$. Prussian blue is soluble in an aqueous solution of oxalic acid, forming blue ink. In air, when exposed to the action of light, it fades; but in the dark it again absorbs oxygen and becomes blue, which fact is also sometimes noticed in blue cloth. An excess of potassium ferrocyanide renders Prussian blue soluble in water, although insoluble in various saline solutions—that is, it converts it into the soluble variety. Strong hydrochloric acid also dissolves Prussian blue.

called 'Gmelin's salt,' because this savant obtained it by the action of chlorine on a solution of the yellow prussiate: $K_4FeC_6N_6 + Cl = K_3FeC_6N_6 + KCl$. The reaction is due to the ferrous salt being changed by the action of the chlorine into a ferric salt. It separates from solutions in anhydrous well-formed prisms of a red colour, but the solution has an olive colour; 100 parts of water, at 10° , dissolve 37 parts of the salt, and at 100° , 78 parts.³⁰ The red prussiate gives a blue precipitate with ferrous salts, called **Turnbull's blue**, very much like Prussian blue (and the soluble variety), because it also contains ferrous cyanide and ferric cyanide, although in another proportion, being formed according to the equation: $3FeCl_2 + 2K_3FeC_6N_6 = 6KCl + Fe_3Fe_2C_{12}N_{12}$, or $3FeC_2N_2, Fe_2C_6N_6$: in Prussian blue we have Fe_7Cy_{18} , and here Fe_5Cy_{12} . A ferric salt ought to form ferric cyanide $Fe_2C_6N_6$, with red prussiate; but ferric cyanide is soluble, and therefore no precipitate is obtained, and the liquid only becomes brown.³¹

³⁰ An excess of chlorine must not be employed in preparing this compound, otherwise the reaction goes further. It is easy to find out when the action of the chlorine on potassium ferrocyanide must cease; it is only necessary to take a sample of the liquid and add a solution of a ferric salt to it. If a precipitate of Prussian blue is formed, more chlorine must be added, as there is still some undecomposed ferrocyanide, for the ferricyanide does not give a precipitate with ferric salts. Potassium ferricyanide, like the ferrocyanide, readily exchanges its potassium for hydrogen and various metals by double decomposition. With the salts of tin, silver, and mercury it forms yellow precipitates, and with those of uranium, nickel, cobalt, copper, and bismuth brown precipitates. The lead salt, under the action of sulphuretted hydrogen, forms lead sulphide and a hydrogen salt or acid, $H_3FeC_6N_6$, corresponding with potassium ferricyanide, which is soluble, crystallises in red needles, and resembles hydroferrocyanic acid, $H_4FeC_6N_6$. Under the action of reducing agents—for instance, sulphuretted hydrogen or copper—potassium ferricyanide is changed into ferrocyanide, especially in the presence of alkalis, and forms a rather energetic **oxidising agent**—capable, for instance, of changing manganeous oxide into dioxide, of bleaching tissues, &c.

³¹ It is important to mention a series of readily crystallisable salts formed by the action of nitric acid on potassium and other ferrocyanides and ferricyanides. These salts contain the elements of nitric oxide, and are therefore called **nitro-**(**nitroso-**) **ferricyanides** (nitro-prussides). Generally a crystalline sodium salt is obtained, $Na_2FeC_5N_5O, 2H_2O$. In its composition this salt differs from the red sodium salt, $Na_3FeC_6N_6$, by the fact that in it one molecule of sodium cyanide, $NaCN$, is replaced by nitric oxide, NO . In order to prepare it, powdered potassium ferrocyanide is mixed with five-sevenths of its weight of nitric acid diluted with an equal volume of water. The mixture is at first left at the ordinary temperature, and then heated on a water-bath. Here ferricyanide is first of all formed (as shown by the liquid giving a precipitate with ferrous chloride), this disappearing later (no precipitate with ferrous chloride), and forming a green precipitate. The liquid, when cooled, deposits crystals of nitre, from which it is then strained off and mixed with sodium carbonate, boiled, filtered, and evaporated; sodium nitrate and the salt described are deposited in crystals. It separates in prisms of a red colour. Alkalis and salts of the alkaline earths do not give precipitates, but soluble compounds, but the salts of iron, zinc, copper, and silver form precipitates in which the sodium is replaced by these metals. It is remarkable that the sulphides of the alkali metals give with this salt an intense bright purple coloration. This

If chlorine and sodium are representatives of independent groups of elements, the same may also be said of iron. Its nearest analogues show, besides a similarity in character, a likeness as regards physical properties and a proximity in atomic weight. Iron occupies a medium position amongst its nearest analogues, with respect both to properties and to the faculty of forming saline oxides, and also as regards atomic weight. On the one hand, cobalt, 59, and nickel, 59, approach iron, 56; they are metals of a more basic character, they do not form stable acids or higher degrees of oxidation, and are a transition to copper, 63, and zinc, 65. On the other hand, manganese, 55, and chromium, 52, forming both basic and acid oxides, are the nearest to iron. In addition to having atomic weights approximately alike, chromium, manganese, iron, cobalt, nickel, and copper have also nearly the same specific gravity, so that the atomic volumes and the molecules of their analogous compounds are also near to one another (see table at the beginning of this volume). Besides this, the likeness between the above-mentioned elements is also seen from the following:

They form suboxides, RO , which are fairly energetic bases, isomorphous with magnesia—for instance, the salt $\text{RSO}_4 \cdot 7\text{H}_2\text{O}$, akin to $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, or to sulphates containing less water; with alkali sulphates all form double salts crystallising with $6\text{H}_2\text{O}$; all are capable of forming ammonium salts, &c. The lower oxides, in the cases of nickel and cobalt, are tolerably stable, and are not easily oxidised (the nickel compound with more difficulty than cobalt, a transition to copper); with manganese, and especially with chromium, they are more easily oxidised than with iron and pass into higher oxides. They all also form oxides of the form R_2O_3 , and with nickel and cobalt, these oxides are very unstable, and are more easily reduced than ferric oxide; but, in the case of chromium, it is very stable, and forms the ordinary kind of salts. Chromium, manganese, and iron are oxidised by alkali and oxidising agents, forming salts like Na_2SO_4 ; but cobalt and nickel are difficult to oxidise, and their acids are not known series of compounds was discovered by Gmelin and studied by Playfair and others (1849).

This series to a certain extent resembles the nitro-sulphide series described by Roussin. Here the primary compound consists of black crystals, which are obtained as follows:—Solutions of potassium hydrosulphide and nitrate are mixed, and the mixture is agitated while ferrie chloride is added, then boiled and filtered; on cooling, **black crystals** are deposited, having the composition $\text{Fe}_6\text{S}_3(\text{NO})_{10} \cdot \text{H}_2\text{O}$ (Rosenberg), or, according to Demel, $\text{FeNO}_2 \cdot \text{NH}_2\text{S}$. They have a slightly metallic lustre, and are soluble in water, alcohol, and ether. They absorb the latter as easily as calcium chloride absorbs water. In the presence of alkalies these crystals remain unchanged, but with acids they evolve nitric oxides. There is no necessity to describe these series in detail, because their connection with other compounds is not yet clear, and they have not yet any application.

with any certainty, and are, in all probability, still less stable than the ferrates. Cr, Mn, and Fe form compounds R_2Cl_6 which are like Fe_2Cl_6 in many respects ; in Co this faculty is weaker and in Ni it has almost disappeared. The cyanogen compounds, especially of manganese and cobalt, are very near akin to the corresponding ferrocyanides. The oxides of nickel and cobalt are more easily reduced to metal than those of iron, but those of manganese and chromium are not reduced so readily as those of iron, and the metals themselves are not easily obtained in a pure state ; they are capable of forming varieties resembling cast iron. The metals Cr, Mn, Fe, Co, and Ni have an iron-grey colour and are very difficult to melt, but nickel and cobalt can be melted in the reverberatory furnace and are more fusible than iron, whilst chromium is more difficult to melt than platinum (Deville). These metals decompose water, but with greater difficulty as the atomic weight rises, forming a transition to copper, which does not decompose water. The **compounds** of all these metals **have various colours**, which are sometimes very bright, especially in the higher stages of oxidation.

These metals of the iron group are often met with together in nature. Manganese nearly everywhere accompanies iron, and iron is always an ingredient in the ores of manganese. Chromium is found principally as chrome ironstone—that is, a peculiar kind of magnetic oxide in which Fe_2O_3 is replaced by Cr_2O_3 .

Nickel and cobalt are as inseparable companions as iron and manganese, and Ni is found with iron in meteorites. The similiarity between them even extends to such remote properties as magnetic qualities. In this series of metals we find those which are the most magnetic : iron, cobalt, and nickel. There is even a magnetic oxide among the chromium compounds, such being unknown in the other series. Nickel easily becomes passive in strong nitric acid. It absorbs hydrogen in just the same way as iron does. In short, in the series Cr, Mn, Fe, Co, and Ni, there are many points in common, although there are many differences, as will be seen still more clearly on becoming acquainted with cobalt and nickel.

In nature **cobalt** is principally found in combination with arsenic and sulphur. *Cobalt arsenide*, or *cobalt speiss*, $CoAs_2$, is found in brilliant crystals of the regular system, principally in Saxony. *Cobalt glance*, $CoAs_2CoS_2$, resembles it very much, and also belongs to the regular system ; it is found in Sweden, Norway, and the Caucasus. *Kupfernickel* is an ore containing nickel and arsenic, but of a different composition from cobalt arsenide, having the formula $NiAs$; it is found in Bohemia and Saxony. It has a copper-red colour and is rarely crystalline ; it is so called because the miners of Saxony first

mistook it for an ore of copper (*Kupfer*), but were unable to extract copper from it. *Nickel glance*, $\text{NiS}_2, \text{NiAs}_2$, corresponding with cobalt glance, is also known. Nickel accompanies the ores of cobalt, and cobalt those of nickel, so that both metals are found together. The ores of cobalt are worked in the Caucasus in the government of Elizavetopolsk. Nickel ores containing aqueous hydrated nickel silicate are found in the Ural (Revdansk). Large quantities of a similar ore are exported into Europe from New Caledonia. Both ores contain about 12 percent. of Ni. *Garnierite*, $(\text{RO})_5(\text{SiO}_2)_4, 1\frac{1}{2}\text{H}_2\text{O}$, where $\text{R}=\text{Ni}$ and Mg , predominates in the New Caledonian ore. Large deposits of nickel have been discovered in Canada, where the ore (as nickeliferous pyrites) is free from arsenic. Cobalt is principally worked up into cobalt compounds, but nickel is generally reduced to the metallic state, in which it is now often used for alloys—for instance, with iron (nickel steel) for coinage in many European States, and for plating other metals, because it does not oxidise in the air. Cobalt arsenide and cobalt glance are principally used for the preparation of cobalt compounds; they are first sorted by discarding the rocky matter, and then roasted. During this process most of the sulphur and arsenic disappears; the arsenious anhydride volatilises with the sulphurous anhydride and the metal also oxidises.³² It is a simple matter to obtain nickel and

³² The residue from the roasting of cobalt ores is called *zaffre*, and is often met with in commerce. From this the purer compounds of cobalt may be prepared. The ores of nickel are also first roasted, and the oxides dissolved in acid, nickelous salts being then obtained.

The further treatment of cobalt and nickel ores is facilitated if the arsenic can be almost entirely removed, which may be effected by roasting the ore a second time with a small addition of nitre and sodium carbonate; the nitre combines with the arsenic, forming an arsenious salt, which may be extracted with water. The remaining mass is dissolved in hydrochloric acid, mixed with a small quantity of nitric acid. Copper, iron, manganese, nickel, cobalt, &c., pass into solution. By passing hydrogen sulphide through the solution, copper, bismuth, lead, and arsenic are deposited as metallic sulphides; but iron, cobalt, nickel, and manganese remain in solution. If an alkaline solution of bleaching powder be then added to the remaining solution, the whole of the manganese will first be deposited in the form of dioxide, then the cobalt as hydrated cobaltic oxide, and finally the nickel also. It is, however, impossible to rely on this method for effecting a complete separation, the more so since the higher oxides of the three above-mentioned metals all have a black colour; but after a few trials it will be easy to find how much bleaching powder is required to precipitate the manganese, and the amount which will precipitate all the cobalt. The manganese may also be separated from cobalt by precipitation from a mixture of the solutions of both metals (in the form of the 'ous' salts) with ammonium sulphide and then treating the precipitate with acetic acid or dilute hydrochloric acid, in which manganese sulphide is easily soluble and cobalt sulphide almost insoluble. Further particulars relating to the separation of cobalt from nickel may be found in treatises on analytical chemistry. In practice it is usual to rely on the rough method of separation founded on the fact that nickel is more easily reduced and more difficult to oxidise than cobalt. The New Caledonian ore is smelted with CaSO_4 and CaCO_3 on coke, and a metallic regulus is obtained containing all the Ni, Fe and S.

cobalt from their oxides. In order to obtain the latter, solutions of their salts are treated with sodium carbonate and the precipitated carbonates are heated ; the suboxides are thus obtained, and these latter are reduced in a stream of hydrogen, or even by heating with ammonium chloride. They easily oxidise when in the state of powder. When the chlorides of nickel and cobalt are heated in a stream of hydrogen, the metal is deposited in brilliant scales. *Nickel is always much more easily and quickly reduced than cobalt*, and, when in a state of powder (reduced by hydrogen), acts in many cases as a contact substance like platinum black. Nickel melts more easily than cobalt, and this even furnishes a means of testing the heating powers of a reverberatory furnace. Cobalt fuses at a temperature only a little lower than that at which iron does. In general, cobalt is more nearly allied to iron than nickel, and the latter more nearly to copper.^{32a} Both nickel and cobalt have magnetic properties like iron, but Co is less magnetic than Fe, and Ni still less so. The specific gravity of nickel reduced by hydrogen is 9·1 and that of cobalt 8·9. Fused cobalt has a specific gravity of 8·5, the density of ordinary nickel being almost the same. Nickel has a greyish silvery-white colour ; it is brilliant and very ductile, so that the finest wire may be easily drawn from it. This wire has a resistance to tension equal to that of iron wire. The beautiful colour of nickel and the high polish which it is capable of receiving and retaining, as it does not oxidise, render it a useful metal for many purposes, and in many ways it resembles silver.^{32b} It is now very common to cover

This is roasted with SiO_2 , which converts all the iron into slag, whilst the Ni remains combined with the S ; this residue on further roasting gives NiO , which is reduced by the carbon to metallic Ni.

For manufacturing purposes somewhat impure cobalt compounds are frequently used, which are converted into **smalt**. This is glass containing a certain amount of cobalt oxide ; the glass acquires a bright blue colour from this addition, so that when powdered it may be used as a blue pigment ; it is also unaltered at high temperatures, so that it used to take the place now occupied by Prussian blue, ultramarine, &c. At present smalt is almost exclusively used for colouring glass and china. To prepare smalt, zaffre is fused in a crucible with quartz and potassium carbonate. A fused mass of cobalt glass is thus formed, and a metallic mass remains at the bottom of the crucible, containing almost all the other metals, arsenic, nickel, copper, silver, &c. This metallic mass is called **speiss**, and is used as nickel ore. Smalt usually contains 70 per cent. of silica, 25 of potash and soda, and about 5 to 6 of cobaltous oxide.

^{32a} All we know respecting the relations of Co and Ni to Fe and Cu confirms the fact that Co is more closely related to Fe and Ni to Cu ; and as the atomic weight of Fe is 56 and that of Cu 63, it would be expected, according to the principles of the periodic system, that the atomic weight of Co would be about 59, whilst that of Ni should be greater than that of Co but less than that of Cu — i.e., about 60. However, as yet the majority of the determinations of the atomic weights of Co and Ni give a different result, but they hardly comply with the desired degree of accuracy, as has been already mentioned in Chap. XV., note 25.

^{32b} For instance, the alkalis may be fused in nickel vessels as well as in silver,

other metals with a layer of nickel (nickel plating). This is done by a process of electro-plating, using a solution of a nickel salt. The colour of cobalt is dark and redder; it is also ductile, and has a greater tensile resistance than iron. Dilute acids act very slowly on nickel and cobalt; nitric acid may be considered as the best solvent for them. The solutions in every case contain salts corresponding with the ferrous salts—that is, the salts CoX_2 , NiX_2 , corresponding with the suboxides of these metals. These salts are similar in their types to those of magnesium and iron. The salts of nickel when crystallising with water have a green colour, and form bright-green solutions, but in the anhydrous state they most frequently have a yellow colour; those of cobalt are generally rose-coloured, and mostly blue when in the anhydrous state. Their aqueous solutions are rose-coloured. Cobaltous chloride is freely soluble in alcohol, and forms a solution of an intense blue colour.³³

If a solution of potassium hydroxide be added to a solution of a

because they have no action upon either metal. Nickel, like silver, is not acted upon by dilute acids. Only nitric acid dissolves both metals well. Nickel is harder, and fuses at a higher temperature than silver. For castings, a small quantity of magnesium (0.001 part by weight) is added to nickel to render it more homogeneous (just as aluminium is added to steel).

³³ The change of colour is dependent in all probability on the combination with water. It enables a solution of cobalt chloride to be used as sympathetic ink. If something be written with cobalt chloride on white paper, it will be invisible on account of the feeble colour of the solution, and when dry nothing can be distinguished. If, however, the paper be heated before the fire, the rose-coloured salt will be changed into a less hydrous blue salt, and the writing will become quite visible, but will fade away when cool.

The change of colour which takes place in solutions of CoCl_2 under the influence not only of solution in water or alcohol, but also of a change of temperature, is a characteristic of all the halogen salts of cobalt. Crystalline iodide of cobalt, $\text{CoI}_2 \cdot 6\text{H}_2\text{O}$, gives a dark-red solution between -22° and $+20^\circ$; above $+20^\circ$ the solution turns brown and passes from olive to green; and from $+35^\circ$ to 320° the solution remains green. According to Étard (1891) the change of colour is due to the fact that at first the solution contains the hydrate $\text{CoI}_2 \cdot 6\text{H}_2\text{O}$, and that above 35° it contains $\text{CoI}_2 \cdot 4\text{H}_2\text{O}$, which can therefore be crystallised from the solutions; the former at ordinary temperature and the latter on heating the solution. A solution of the hexahydrated chloride of cobalt, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, is rose-coloured between -22° and $+25^\circ$; but the colour changes at $+25^\circ$, and passes through all the tints between red and blue up to 50° ; a true blue solution is only obtained at 55° , and this colour remains up to 300° . This true blue solution contains a hydrate, $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ or $\text{CoCl}_2 \cdot \text{H}_2\text{O}$, according to Potilitzin.

This is similar to what we have repeatedly seen—that aqueous solutions (for instance, Chap. XXII., note 23, for Fe_2Cl_6) deposit different crystallo-hydrates at different temperatures, and that the amount of water in the hydrate decreases as the temperature t rises. Nor is it exceptional that the colour of a salt varies according as it contains different amounts of H_2O . But in this instance it is characteristic that the change of colour takes place in solution in the presence of an excess of water. This apparently shows that the actual solution may contain either $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ or $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$. And as we know that a solution may contain both metaphosphoric, PHO_3 , and orthophosphoric acid, $\text{H}_3\text{PO}_4 = \text{HPO}_3 + \text{H}_2\text{O}$, as well as certain other anhydrides, the question of the state

cobalt salt, a blue precipitate of the basic salt will be formed. If a solution of a cobalt salt be heated almost to the boiling-point, and the solution be then mixed with a boiling solution of an alkali hydroxide, of substances in solutions becomes still more complicated (see the salts of Cr_2O_3). Perhaps the rose-tint is peculiar to $\text{CoX}_2, n\text{H}_2\text{O}$ and the blue to $\text{Co}(\text{OH})_2\text{HX}$?

It is remarkable that a solution of cobalt nitrate acts, as has long been known, as an antidote in cases of poisoning by prussic acid or potassium cyanide.

Nickel sulphate crystallises from neutral solutions at a temperature of from 15° to 20° in *rhombic* crystals containing $7\text{H}_2\text{O}$. Its form approaches very closely to that of the salts of zinc and magnesium. The planes of a vertical prism for magnesium salts are inclined at an angle of $90^\circ 30'$, for zinc salts at an angle of $91^\circ 7'$, and for nickel salts at an angle of $91^\circ 10'$. Such is also the form of the zinc and magnesium selenates and chromates. Cobalt sulphate containing 7 molecules of water is deposited in crystals of the *monoclinic* system, like the corresponding salts of iron and manganese. The angle of a vertical prism for the iron salt is $82^\circ 20'$, for cobalt, $82^\circ 22'$, and the inclination of the horizontal pinacoid to the vertical prism for the iron salt is $99^\circ 2'$, and that for the cobalt salt, $99^\circ 36'$. All the isomorphous mixtures of the salts of magnesium, iron, cobalt, nickel and manganese have the same form if they contain 7 mols. of H_2O and iron or cobalt predominate, whilst if there is a preponderance of magnesium, zinc, or nickel, the crystals have a rhombic form like magnesium sulphate. Hence these sulphates are **dimorphous**, but for some the one form is more stable and for others the other. Brooke, Moss, Mitscherlich, Rammelsberg, and Marignac have explained these relations. Brooke and Mitscherlich also supposed that $\text{NiSO}_4, 7\text{H}_2\text{O}$ is capable of assuming not only these forms, but also that of the *tetragonal* system, because it is deposited in this form from acid, and especially from slightly heated, solutions (30° to 40°). But Marignac demonstrated that the tetragonal crystals do not contain 7, but 6, molecules of water, $\text{NiSO}_4, 6\text{H}_2\text{O}$. He also observed that a solution evaporated at 50° to 70° deposits monoclinic crystals, but of a different form from those of ferrous sulphate, $\text{FeSO}_4, 7\text{H}_2\text{O}$ —the angle of the prism being $71^\circ 52'$, that of the pinacoid, $95^\circ 6'$. This salt appears to be the same with 6 molecules of water as the tetragonal. Marignac also obtained magnesium and zinc salts with 6 molecules of water by evaporating their solutions at a higher temperature, and these salts were found to be isomorphous with the monoclinic nickel salt. In addition to this it must be observed that the rhombic crystals of nickel sulphate with $7\text{H}_2\text{O}$ become turbid under the influence of heat and light, lose water, and change into the tetragonal salt. The monoclinic crystals in time also become turbid, and change their structure, so that the tetragonal form of this salt is the most stable. We may also add that nickel sulphate in all its shapes forms very beautiful emerald-green crystals, which, when heated to 230° , assume a dirty greenish-yellow hue and then contain one molecule of water.

It may also be added that when equivalent aqueous solutions of NiX_2 (green) and CoX_2 (red) are mixed together they give an almost colourless (grey) solution, in which the green and red colours of the component parts disappear owing to the combination of the complementary colours (Chap. XXI., note 23).

A double salt NiKF_3 is obtained by heating NiCl_2 with KFHF in a platinum crucible; KCoF_3 is formed in a similar manner. The nickel salt occurs in fine green plates, easily soluble in water, but scarcely at all in ethyl or methyl alcohol. They decompose into green oxide of nickel and potassium fluoride when heated in a current of air. The analogous salt of cobalt crystallises in crimson flakes.

Crystalline fluoride of nickel, NiF_2 , obtained by heating the amorphous powder formed by decomposing the double ammonium salt in a stream of hydrofluoric acid, occurs in beautiful green prisms, sp. gr. 4.63, which are insoluble in water, alcohol, or ether; sulphuric, hydrochloric, and nitric acids also have no action upon them, even when heated; NiF_2 is decomposed by steam, with the formation of black oxide, which retains the crystalline structure of the salt. Fluoride of cobalt, CoF_2 (sp. gr. 4.4), resembles NiF_2 , but fuses (1400°) with greater difficulty (Poulenc, 1892).

a pink precipitate of cobaltous hydroxide, $\text{Co}(\text{H}_2\text{O})_2$, will be formed. If air be not completely excluded during the precipitation by boiling, the precipitate will also contain brown cobaltic hydroxide formed by the further oxidation of the cobaltous oxide.³⁴ Under similar circumstances nickel salts form a green precipitate of nickelous hydroxide, $\text{Ni}(\text{OH})_2$, the formation of which is not hindered by the presence of ammonium salts, but in that case only requires more alkali to completely separate the nickel. The nickelous oxide obtained, either by heating the hydroxide, or from the carbonate or nitrate, is a grey powder, readily soluble in acids and easily reduced; but the same substance may be obtained in the crystalline form as an ordinary product from the ores; it crystallises in regular octahedra, with a metallic lustre, and is of a grey colour. In this state the nickelous oxide almost resists the action of acids.^{34a}

It is interesting to note the relation of the cobaltous and nickelous hydroxides to ammonia; aqueous ammonia dissolves the precipitated cobaltous and nickelous hydroxides. The blue ammoniacal solution of nickel resembles a similar solution of cupric oxide, but has a somewhat reddish tint. It is characterised by the fact that it dissolves silk in

³⁴ Hydrated suboxide of cobalt (de Schulten, 1889) is obtained by heating a solution of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ with caustic potash in a stream of coal gas. The hydrate which separates out dissolves in the caustic potash and forms a dark-blue solution. On leaving the solution to stand for 24 hours in atmosphere of coal gas (in order to prevent oxidation), $\text{Co}(\text{OH})_2$ separates out as a violet powder, which is seen to be crystalline under the microscope. The specific gravity of this hydrate is 3.597 at 15°. It does not undergo change in the air; warm acetic acid dissolves it, but it is insoluble in either hot or cold solutions of ammonia and sal-ammoniac.

^{34a} Potassium cyanide forms a precipitate with cobalt salts which is soluble in an excess of the reagent and forms a green solution. On heating this and adding a certain quantity of acid, a double cobalt cyanide is formed which corresponds with potassium ferri-cyanide. Its formation is accompanied with the evolution of hydrogen, and is founded upon the property which cobalt has of oxidising in an alkaline solution, the development of which has been observed in such a considerable measure in the cobaltamine salts (see note 35). The process which goes on here may be expressed as follows: $\text{CoC}_2\text{N}_2 + 4\text{KCN}$ first forms $\text{CoK}_4\text{C}_6\text{N}_6$, which salt with water, H_2O , forms potassium hydroxide, KHO , hydrogen, H , and the salt, $\text{K}_3\text{CoC}_6\text{N}_6$. Here naturally the presence of the acid is indispensable in consequence of its being required to combine with the alkali. From aqueous solutions this salt crystallises in transparent hexagonal prisms of a yellow colour, readily soluble in water. The reactions of double decomposition, and even the formation of the corresponding acid, are here exactly the same as in the case of the ferri-cyanide. If a nickelous salt be treated in precisely the same manner as that just described for a salt of cobalt, decomposition will occur. A similar relation is exhibited by CoX_2 in reacting with an excess of sodium nitrite, when $\text{Na}_3\text{Co}(\text{NO}_2)_6$ is formed in the solution (acidulated with acetic acid) and NO , proceeding from the oxidation of CoX_2 into CoX_3 , is evolved. This sodium salt dissolves easily in water, but the corresponding potassium salt (also the Rb and Cs salts) are only slightly soluble (less so than the platinichlorides), so that sodium may be separated from potassium by this means. These double nitro-cobaltic salts are stable, and in general closely resemble the ferri-cyanides. Nickel does not form such compounds.

the same way as ammoniacal cupric oxide dissolves cellulose. Ammonia likewise dissolves the precipitate of cobaltous hydroxide, forming a brownish liquid, which becomes darker in air and finally assumes a bright-red hue, absorbing oxygen. The admixture of ammonium chloride prevents the precipitation of cobalt salts by ammonia; when the ammonia is added, a brown solution is obtained from which, as in the case of the preceding solution, potassium hydroxide does not separate the cobaltous oxide. Peculiar compounds are produced in this solution; they are comparatively stable, containing ammonia and an excess of oxygen; they bear the name cobaltoamine and cobaltamine salts. They have been principally investigated by Genth, Frémy, Jörgensen, Werner, and others. Genth found that when a cobalt salt, mixed with an excess of ammonium chloride, is treated with ammonia and exposed to the air, after a certain lapse of time, on adding hydrochloric acid and boiling, a red powder is precipitated and the remaining solution contains an orange salt. The study of these compounds led to the discovery of a whole series of similar salts, some of which correspond with particular higher degrees of oxidation of cobalt, which are described later.³⁵

³⁵ The cobalt salts may be divided into at least the following classes, which repeat themselves for Cr, Ir, Rh (we shall not stop to consider the latter, particularly as they closely resemble the cobalt salts), &c., and Jörgensen and Werner in 1897 and the neighbouring years added much to our knowledge of these complex compounds.

(a) **Ammonium cobalt salts**, which are simply direct compounds of the cobaltous salts, CoX_2 , with ammonia, similar to various other compounds of the salts of silver, copper, and even calcium and magnesium, with ammonia. They are easily crystallised from an ammoniacal solution, and have a pink colour. Thus, for instance, when cobaltous chloride in solution is mixed with sufficient ammonia to redissolve the precipitate first formed, octahedral crystals are deposited which have a composition $\text{CoCl}_2 \cdot \text{H}_2\text{O} \cdot 6\text{NH}_3$. These salts are nothing else than combinations with ammonia of crystallisation—if it may be so termed—likening them in this way to combinations with water of crystallisation. This similarity is evident both from their composition and from their capability of giving off ammonia at various temperatures. The most important point to observe is that all these salts contain 6 molecules of ammonia to 1 atom of cobalt, and that this ammonia is held in fairly stable connection. Water decomposes these salts. (Nickel behaves similarly without forming other compounds corresponding to the true cobaltic.)

(b) The solutions of the above-mentioned salts are rendered turbid by the action of the air; they absorb oxygen and in strong solutions become covered with a crust of **oxycobaltamine salts**. The latter are sparingly soluble in aqueous ammonia, have a brown colour, and are characterised by the fact that with warm water they **evolve oxygen**, forming salts of the following category: The nitrate may be taken as an example of this kind of salt; its composition is $\text{CoN}_2\text{O}_7 \cdot 5\text{NH}_3 \cdot \text{H}_2\text{O}$. It differs from cobaltous nitrate, $\text{Co}(\text{NO}_3)_2$, in containing an extra atom of oxygen—that is, it corresponds with cobalt dioxide, CoO_2 , in the same way that the first salts correspond with cobaltous oxide; they contain 5, and not 6, molecules of ammonia, as if NH_3 had been replaced by O, but we shall afterwards meet compounds containing either 5NH_3 or 6NH_3 to each atom of cobalt.

(c) **The luteocobaltic salts** are thus called because they have a yellow (luteus) colour. They are obtained from the salts of the first kind by submitting them in dilute

Nickel does not possess this property of absorbing the oxygen of the air when in ammoniacal solution. In order to understand this distinc-

solution to the action of the air; in this case salts of the second kind are not formed, because they are decomposed by an excess of water, with the evolution of oxygen and the formation of luteocobaltic salts. By the action of ammonia the salts of the fifth kind (roseocobaltic) are also converted into luteocobaltic salts. These last-named salts generally crystallise readily, and have a yellow colour; they are comparatively much more stable than the preceding ones, and for a certain time resist even the action of boiling water. Boiling aqueous potash liberates ammonia and precipitates hydrated cobaltic oxide, $\text{Co}(\text{OH})_2$, from them. This shows that the luteocobaltic salts correspond with cobaltic oxide, CoX_3 , and those of the second kind with the dioxide. When a solution of luteocobaltic sulphate, $\text{Co}_2(\text{SO}_4)_3 \cdot 12\text{NH}_3 \cdot 4\text{H}_2\text{O}$, is treated with baryta, barium sulphate is precipitated, and the solution contains luteocobaltic hydroxide, $\text{Co}(\text{OH})_3 \cdot 6\text{NH}_3$, which is soluble in water, is powerfully alkaline, absorbs the oxygen of the air, and when heated is decomposed with the evolution of ammonia. The luteocobaltic salts again contain 6NH_3 to each atom of cobalt, like the salts of the first kind. In the luteo-salts all the X's react (are ionised, as some chemists say) as in ordinary salts—for instance, all the Cl_3 is precipitated by a solution of AgNO_3 ; all the $(\text{SO}_4)_3$ gives a precipitate with BaX_2 , &c. The double salt formed with PtCl_4 is composed in the same manner as the potassium salt (K_2PtCl_6), that is, it has the composition $(\text{CoCl}_3 \cdot 6\text{NH}_3)_2 \cdot 3\text{PtCl}_4$, the amount of chlorine in the PtCl_4 being double that in the alkaline salt.

In the rosepentamine (e), and rosetetramine (f), salts also, all the X's react or are ionised, but in the (g) and (h) salts only a portion of the X's react, and they are equal to the (e) and (f) salts minus water; this means that although the water dissolves them it is not combined with them, as PHO_3 differs from PH_3O_3 ; phenomena of this class correspond exactly to what has been already (Chap. XXI., note 7) mentioned respecting the green and violet salts of oxide of chromium.

(d) **The fuscocobaltic salts.**—An ammoniacal solution of cobalt salts acquires a brown colour in the air, due to the formation of these salts. They are also produced by the decomposition of salts of the second kind; they crystallise badly, and are separated from their solutions by addition of alcohol or an excess of ammonia. When boiled they give up the ammonia and cobaltic oxide which they contain. Hydrochloric and nitric acids give a yellow precipitate with these salts, which turns red when boiled, forming salts of the next category. The following formulæ represent the compositions of two of the fuscocobaltic salts: $\text{Co}_2\text{O}(\text{SO}_4)_2 \cdot 8\text{NH}_3 \cdot 4\text{H}_2\text{O}$ and $\text{Co}_2\text{OCl}_4 \cdot 8\text{NH}_3 \cdot 3\text{H}_2\text{O}$. It is evident that the fuscocobaltic salts correspond to the ammoniacal compounds of basic cobaltic salts. The normal cobaltic sulphate ought to have the composition $\text{Co}_2(\text{SO}_4)_3 = \text{Co}_2\text{O}_3 \cdot 3\text{SO}_3$; the simplest basic salts will be $\text{Co}_2\text{O}(\text{SO}_4)_2 = \text{Co}_2\text{O}_3 \cdot 2\text{SO}_3$, and $\text{Co}_2\text{O}_2(\text{SO}_4) = \text{Co}_2\text{O}_3 \cdot \text{SO}_3$. The fuscocobaltic salts correspond with the first type of basic salts. They are changed (in concentrated solutions) into oxycobaltamine salts by absorption of one atom of oxygen, $\text{Co}_2\text{O}_2(\text{SO}_4)_2$. Under many conditions the salts of fuscocobalt are easily transformed into salts of the next series. The salts of the series that has just been described contain 4 molecules of ammonia to 1 atom of cobalt.

(e) **The roseocobaltic** (or rosepentamine or aquapentaminocobaltic) salts, $\text{CoX}_2\text{H}_2\text{O} \cdot 5\text{NH}_3$, like the luteocobaltic, correspond to CoX_3 , but contain less ammonia, and an extra molecule of water. Thus the sulphate is obtained from cobaltous sulphate dissolved in ammonia and left exposed to the air until transformed into a brown solution of the fuscocobaltic salt; when this is treated with sulphuric acid a crystalline powder of the roseocobaltic salt, $\text{Co}_2(\text{SO}_4)_3 \cdot 10\text{NH}_3 \cdot 5\text{H}_2\text{O}$, separates. This salt forms tetragonal crystals of a red colour, only slightly soluble in cold, but readily in warm water. When the sulphate is treated with baryta, roseocobaltic hydroxide is formed in the solution, which absorbs the carbonic anhydride of the air. It is obtained from the next series by the action of alkalis.

(f) **The rosetetramine cobaltic salts**, $\text{CoCl}_3 \cdot 2\text{H}_2\text{O} \cdot 4\text{NH}_3$, were obtained by Jörgensen, and belong to the type of the luteo-salts, only with the substitution of 2NH_3 for H_2O

tion, and in general the relation of nickel, it is important to observe that cobalt more easily forms a higher degree of oxidation—namely,

Like the luteo- and roseo-salts they give double salts with PtCl_4 , similar to the alkaline double salts, for instance, $(\text{Co}_2\text{H}_2\text{O}_4\text{NH}_3)_2(\text{SO}_4)_2\text{Cl}_2, \text{PtCl}_4$. They are darker in colour than the preceding, but also crystallise well. They are formed by dissolving CoCO_3 in sulphuric acid (of a given strength), and after NH_3 and carbonate of ammonium have been added, air is passed through the solution (for oxidation) until the latter turns red. It is then evaporated with lumps of carbonate of ammonium, filtered from the precipitate, and crystallised. A salt of the composition $\text{Co}_2(\text{CO}_3)_2(\text{SO}_4)(2\text{H}_2\text{O}_4\text{NH}_3)_2$ is thus obtained, from which the other salts may be easily prepared.

(g) The **purpureocobaltic salts** (pentamine), $\text{CoX}_3 \cdot 5\text{NH}_3$, are also products of the direct oxidation of ammoniacal solutions of cobalt salts. They are easily obtained by heating the roseocobaltic and luteo-salts with strong acids. They are to all effect the same as the roseocobaltic salts, only anhydrous. Thus, for instance, the purpureocobaltic chloride, $\text{Co}_2\text{Cl}_6 \cdot 10\text{NH}_3$, or $\text{CoCl}_3 \cdot 5\text{NH}_3$, is obtained by boiling the oxycobaltamine salts with ammonia. There is the same distinction between these salts and the preceding ones as between the various compounds of cobaltous chloride with water. In the purpureocobaltic only X_2 out of the X_3 react (are ionised). To the rosetetramine salts (f) there correspond the **purpureotetramine salts**, $\text{CoX}_3 \cdot \text{H}_2\text{O} \cdot 4\text{NH}_3$. The corresponding chromium purpureopentamine salt, $\text{CrCl}_3 \cdot 5\text{NH}_3$ is obtained with particular ease (Christensen, 1893). Dry anhydrous chromium chloride is treated with anhydrous liquid ammonia in a freezing mixture composed of liquid CO_2 and chlorine, and after some time the mixture is taken out of the freezing mixture, so that the excess of NH_3 boils away; the violet crystals then immediately acquire the red colour of the salt, $\text{CrCl}_3 \cdot 5\text{NH}_3$, which is formed. The product is washed with water (to extract the luteo-salt, $\text{CrCl}_3 \cdot 6\text{NH}_3$), which does not dissolve the salt, and it is then recrystallised from a hot solution of hydrochloric acid.

(h) The **praseocobaltic salts**, $\text{CoX}_3 \cdot 4\text{NH}_3$, are green, and form, with respect to the rosetetramine salts (f), the products of ultimate dehydration (for example, like metaphosphoric acid with respect to orthophosphoric acid), but in dissolving in water they give neither rosetetramine nor tetramine salts. (In my opinion one should expect salts with a still smaller amount of NH_3 , but with H_2O and having the blue colour proper to the low-hydrated compounds of cobalt; the green colour of the praseo-salts already forms a step towards the blue). Jürgensen obtained salts for ethylene-diamine, $\text{N}_2\text{H}_4\text{C}_2\text{H}_4$, which replaces 2NH_3 . After being kept a long time in aqueous solution they give rosetetramine salts, just as metaphosphoric acid gives orthophosphoric acid, while the rosetetramine salts are converted into praseo-salts by Ag_2O and NaHO . Here only one X is ionised out of the X_3 . There are also basic salts of the same type; but the best known is the chromium salt called the rhodozochromic salt, $\text{Cr}_2(\text{OH})_3\text{Cl}_3 \cdot 6\text{NH}_3 \cdot 2\text{H}_2\text{O}$, which is formed by the prolonged action of water upon the corresponding roseo-salt.

The **ammonio-metallic salts** present a most complete qualitative and quantitative resemblance to the **hydrated salts of metals**. The composition of the latter is $\text{MX}_n \cdot m\text{H}_2\text{O}$, where M = metal, X = the haloid, simple or complex, and n and m the quantities of the haloid and so-called water of crystallisation respectively. The composition of the ammoniacal salts of metals is $\text{MX}_n \cdot m\text{NH}_3$. The water of crystallisation is held by the salt with more or less stability, and some salts even do not retain it at all; some part with water easily when exposed to the air, others when heated, and then only with difficulty. In the case of some metals all the salts combine with water, whilst with others only a few, and the water so combined may then be easily disengaged. All this applies equally well to the ammoniacal salts, and therefore the combined ammonia may be termed the **ammonia of crystallisation**. Just as the water which is combined with a salt is held by it with different degrees of force, so it is with ammonia. In combining with 2NH_3 , PtCl_2 evolves 31,000 cal.; while CaCl_2 only evolves 14,000 cal.; and the former compound parts with its NH_3 (together with HCl in this case) with more difficulty and only above 200° , while the latter disengages ammonia at 180° . The amount

sesquioxide of cobalt, **cobaltic oxide**, Co_2O_3 —than nickel, especially in the presence of hypochlorous acid. If a solution of a cobalt salt be

of combined ammonia is as variable as the amount of water of crystallisation; for instance, $\text{SnI}_4, 8\text{NH}_3$; $\text{CrCl}_2, 8\text{NH}_3$; $\text{CrCl}_3, 6\text{NH}_3$; $\text{CrCl}_3, 5\text{NH}_3$; $\text{PtCl}_2, 4\text{NH}_3$; &c., are known. Very often NH_3 is replaceable by OH_2 and conversely. A colourless anhydrous cupric salt—for instance, cupric sulphate—forms blue and green salts when combined with water, and violet when combined with ammonia. If steam is passed through anhydrous copper sulphate the salt absorbs water and becomes heated; if ammonia is substituted for the water the heating becomes much more intense, and the salt breaks up into a fine violet powder. With water, $\text{CuSO}_4, 5\text{H}_2\text{O}$ is formed, and with ammonia $\text{CuSO}_4, 5\text{NH}_3$, the number of water and ammonia molecules retained by the salt being the same in each case, and as a proof of this, and that it is not an isolated coincidence, the remarkable fact must be borne in mind that water and ammonia consecutively, molecule for molecule, are capable of supplanting each other, and forming the compounds $\text{CuSO}_4, 5\text{H}_2\text{O}$; $\text{CuSO}_4, 4\text{H}_2\text{O}, \text{NH}_3$; $\text{CuSO}_4, 3\text{H}_2\text{O}, 2\text{NH}_3$; $\text{CuSO}_4, 2\text{H}_2\text{O}, 3\text{NH}_3$; $\text{CuSO}_4, \text{H}_2\text{O}, 4\text{NH}_3$, and $\text{CuSO}_4, 5\text{NH}_3$. The last of these compounds was obtained by Heinrich Rose, and my experiments have shown that more ammonia than this cannot be retained. By adding to a strong solution of cupric sulphate sufficient ammonia to dissolve the whole of the oxide precipitated, and then adding alcohol, Berzelius obtained the compound $\text{CuSO}_4, \text{H}_2\text{O}, 4\text{NH}_3$, &c. The law of substitution also assists in reuderer these phenomena clearer, because a compound of ammonia with water forms ammonium hydroxide, NH_4HO , and therefore these molecules combining with one another may also interchange, as being of equal value. And as ammonia is capable of combining with acids, and as some of the salts formed by slightly energetic bases in their properties more closely resemble acids (that is, salts of hydrogen) than others, we might expect to find more stable and more easily formed ammonio-metallic salts with metals and their oxides, having weaker basic properties than with those which form energetic bases. This explains why the salts of potassium, barium, &c., do not form ammonio-metallic salts, whilst the salts of silver, copper, zinc, &c., easily form them, and the salts RX_3 still more easily and with greater stability. This consideration also accounts for the great stability of the ammoniacal compounds of cupric oxide compared with those of silver oxide, since the former is displaced by the latter. It also enables us to see clearly the distinction which exists between the stability of the cobaltamine salts containing salts correspondng with cobaltous oxide, and that of those corresponding with higher oxides of cobalt, for the latter are weaker bases than cobaltous oxides. *The nature of the forces and quality of the phenomena occurring during the formation of the most stable substances, and of such compounds as crystallisable compounds, are one and the same, although perhaps exhibited in a different degree.* This, in my opinion, may be best confirmed by examining the compounds of carbon, because for this element the nature of the forces acting during the formation of its compounds is well known. Let us take as an example two unstable compounds of carbon. Acetic acid, $\text{C}_2\text{H}_4\text{O}_2$ (specific gravity 1.06), forms with water the hydrate, $\text{C}_2\text{H}_4\text{O}_2, \text{H}_2\text{O}$, denser (1.07) than either of the components, but unstable and easily decomposed, and generally simply referred to as a solution. Such also is the crystalline compound of oxalic acid, $\text{C}_2\text{H}_2\text{O}_4$, with water, $\text{C}_2\text{H}_2\text{O}_4, 2\text{H}_2\text{O}$. Their formation might be predicted as starting from the hydrocarbon C_2H_6 , in which, as in any other, the hydrogen may be exchanged for chlorine, the water residue (hydroxyl), &c. The first substitution product with hydroxyl, $\text{C}_2\text{H}_5(\text{HO})$, is stable; it can be distilled without alteration, resists a temperature higher than 100° , and then does not give off water. This is ordinary alcohol. The second, $\text{C}_2\text{H}_4(\text{HO})_2$, can also be distilled without change, but can be decomposed into water and $\text{C}_2\text{H}_4\text{O}$ (ethylene oxide or aldehyde); it boils at about 197° , whilst the first hydrate boils at 78° , a difference of about 100° . The compound $\text{C}_2\text{H}_3(\text{HO})_3$ will be the third product of such substitution; it ought to boil at about 300° , but does not resist this temperature—it decomposes into H_2O and $\text{C}_2\text{H}_2\text{O}_2$. The above-mentioned hydrate of acetic acid is such a decomposable hydrate—that is to say, what is called a solution. Still less stability

mixed with barium carbonate and an excess of hypochlorous acid be added, or chlorine gas be passed through it, then at the ordinary

may be expected from the following hydrates forming glycollic, $C_2H_4O_3$, and glyoxylic, $C_2H_4O_4$, acids. The last hydrate, which ought to be obtained from $C_2H_6O_3$, and ought to have the composition $C_2(HO)_6$, is the crystalline compound of oxalic acid, $C_2H_2O_4$ (two hydroxyl groups), and water, $2H_2O$, which has been already mentioned. The hydrate $C_2(HO)_6 = C_2H_2O_4 \cdot 2H_2O$, ought, according to the foregoing reasoning, to boil at about 600° , but it does not resist this temperature, but at a much lower point splits up into water, $2H_2O$, and the hydrate $C_2O_2(HO)_2$, which is also capable of yielding water. Without going into further discussion of this subject, it may be observed that the formation of the hydrates, or compounds with water of crystallisation, of acetic and oxalic acids has thus received an accurate explanation, illustrating the point we desired to prove in affirming that compounds with water of crystallisation are held together by the same forces as those which act in the formation of other complex substances, and that the easy displaceability of the water of crystallisation is only a peculiarity of a local character, and not a radical point of distinction. Hence the forces which induce salts to combine with nH_2O or with nNH_3 are undoubtedly of the same order as the forces which govern the formation of ordinary 'atomic' and saline compounds. [A great impediment in the study of the former was caused by the conviction which reigned in the sixties and seventies, that 'atomic' were essentially different from 'molecular' compounds like crystallohydrates, in which it was assumed that there was a combination of entire molecules, as though without the participation of the atomic forces.] If the bonds between chlorine and different metals are not equally strong, so also the bond uniting nH_2O and nNH_3 is exceedingly variable; there is nothing very surprising in this. And in the fact that the combination of different amounts of NH_3 and H_2O alters the capacity of the haloids X of the salts RX_3 for reaction (for instance, in the luteo-salts all the X_3 , while in the purpureo-, only 2 out of the 3, and in the praseo-salts only 1 of the 3 X 's reacts), we should see, above all, a phenomenon similar to that known for many complex compounds, for organic compounds and for Cr_2Cl_6 (Chap. XXI, note 7a), for in both instances the essence of the difference lies in the removal of water; a molecule $ReCl_3 \cdot 6H_2O$ or $ReCl_3 \cdot 6NH_3$ contains the halogen in a perfectly mobile (ionised) state, while in the molecule $ReCl_3 \cdot 5H_2O$ or $ReCl_3 \cdot 5NH_3$ a portion of the halogen has almost lost its faculty for reacting with $AgNO_3$, just as metalepsical chlorine has lost this faculty which is fully developed in the chloranhydride. Until the reason of this difference be clear, we cannot expect that ordinary points of view and generalisation can give a clear answer. However, we may assume that the explanation here lies in the nature and kind of motion of the atoms in the molecules, although as yet it is not clear how. Nevertheless, I think it well to call attention again (Chap. I.) to the fact that the combination of water, and hence, also, of any other element, leads to most diverse consequences; the water in the gelatinous hydrate of alumina or in the decahydrated Glauber's salt is very mobile, and easily reacts like water in a free state; but the same water combined with oxide of calcium, or C_2H_4 (for instance, in C_2H_6O and in $C_4H_{10}O$), or with P_2O_5 , has become quite different, and no longer acts like water in a free state. The chlorine in chlorates no longer gives a precipitate of chloride of silver with $AgNO_3$. Thus, although the instance which is found in the difference between the rosco- and purpureo-salts deserves to be fully studied on account of its simplicity, still it is far from being exceptional, and we cannot expect it to be thoroughly explained unless a mass of similar instances, which are exceedingly common among chemical compounds, be conjointly explained.

Kournakoff (1894) showed that at 0° the solubility of the lutco-salt, $CoCl_3 \cdot 6NH_3$, is 4.30 (per 100 of water), and at 20° , 7.7; that in passing into the roseo-salt, $CoCl_3 \cdot H_2O \cdot 5NH_3$, the solubility rises considerably, and at 0° is 16.4, and at 20° , about 27, whilst the passage into the purpureo-salt, $CoCl_3 \cdot 5NH_3$, is accompanied by a great fall in the solubility, which then has the value 0.23 at 0° and about 0.5 at 20° . And as crystallohydrates with a smaller amount of water are usually more soluble than the higher crystallohydrates (Le Chatelier), whilst here we find that the solubility falls (in the purpureo-salt) with a loss

temperature, the whole of the cobalt will be separated, on shaking, in the form of black cobaltic oxide: $2\text{CoSO}_4 + \text{ClHO} + 2\text{BaCO}_3 = \text{Co}_2\text{O}_3 + 2\text{BaSO}_4 + \text{HCl} + 2\text{CO}_2$. Under these circumstances, nickelous oxide does not immediately form black sesquioxide, but after a considerable space of time it also separates in the form of sesquioxide, Ni_2O_3 , but always later than with cobalt, which shows the relative difficulty of further oxidation of the nickelous oxide. It is, however, possible to oxidise it; if, for instance, the hydroxide, NiH_2O_2 , be shaken in water and chlorine gas be passed through it, then nickel chloride, which is soluble in water, will be formed, together with insoluble nickelic oxide in the form of a black precipitate: $3\text{NiH}_2\text{O}_2 + \text{Cl}_2 = \text{NiCl}_2 + \text{Ni}_2\text{O}_3 + 3\text{H}_2\text{O}$. Nickelic oxide may also be obtained by adding sodium hypochlorite mixed with alkali to a solution of a nickel salt. Nickelic and cobaltic hydrates are black. Nickelic oxide evolves oxygen with all acids, and in consequence of this is not separated as a precipitate in the presence of acids; thus, it evolves chlorine with hydrochloric acid, exactly like manganese dioxide. When nickelic oxide is dissolved in aqueous ammonia it liberates nitrogen, and ammoniacal solution of nickelous oxide is formed. When heated, nickelic oxide loses oxygen, forming nickelous oxide. Cobaltic oxide, Co_2O_3 , exhibits more stability than nickelic oxide, and shows feeble basic properties; it is dissolved by acetic acid without the evolution of oxygen.^{35a} But ordinary acids, especially on heating, evolve oxygen, forming a solution of a cobaltous salt. The presence of a cobaltic salt in a solution of a cobaltous salt may be detected by the brown colour of the solution and the black precipitate formed by the addition of alkali, and also from the fact that such solutions evolve chlorine when heated with hydrochloric acid. Cobaltic oxide may be prepared not only by the above-mentioned methods, but also by heating cobalt nitrate, after which a steel-coloured mass remains which retains traces of nitric acid, but when further heated to incandescence evolves oxygen, leaving a compound of cobaltic and cobaltous oxides, similar to magnetic ironstone. Cobalt (but not nickel) undoubtedly forms, besides Co_2O_3 , a dioxide, CoO_2 . This is obtained ³⁶

of water, it follows that the water contained in the roseo-salt cannot be compared with water of crystallisation. Kournakoff, therefore, connects the fall in solubility (in the passage of the roseo- into the purpureo-salts) with the accompanying loss in the reactive capacity of the chlorine.

^{35a} Marshall (1891) obtained cobaltic sulphate, $\text{Co}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, by the action of an electric current upon a strong solution of CoSO_4 .

³⁶ According to Schroeder and Carnot, the precipitate produced by the hypochlorites has a composition $\text{Co}_{10}\text{O}_{16}$, whilst the oxide given by iodine in the presence of an alkali contains a larger amount of oxygen. Vortmann (1891) reinvestigated the composition of the higher oxygen oxide obtained by iodine in the presence of alkali, and found that the greenish precipitate (which disengages oxygen even when heated to only 100°)

when the cobaltous oxide is oxidised by iodine or peroxide of barium.³⁷

Nickel alloys possess qualities which render them valuable for technical purposes, the alloy of nickel with iron being particularly remarkable. This alloy is met with in nature as **meteoric iron**. The Pallasoffsky mass of meteoric iron, preserved in the St. Petersburg Academy, fell in Siberia in the last century; it weighs about 15 cwt. and contains 88 per cent. of iron, about 10 of nickel, together with a small admixture of other metals. The addition of a small amount of Ni to iron and steel increases their strength and elasticity, so that nickel steel containing up to 3 per cent. (but not more than 10 per cent.) of Ni is frequently used for making armour plates, and for other purposes. The alloys of Fe and Ni have acquired great theoretical and practical interest since Guillaume (1898) carried on his systematic researches at the Bureau of Weights and Measures (at Breteuil, near Paris) on these alloys, more especially on the coefficient of expansion and the capacity for magnetism. He found that the alloy containing about 28 per cent. Ni (probably NiFe_3 , requiring 26.0 per cent. Ni) does not become magnetised. But what is still more remarkable is that the alloys containing about 35 per cent. of Ni (probably NiFe_2 , which contains 34.5 per cent. of Ni) have exceedingly small coefficients of linear expansions (per 1°C.), namely, about 0.000,000,90, that is, less than that of the alloy containing 10 per cent. of iridium and 90 of platinum, which has the value 0.000,008,67, or those of iron or steel (0.000,010,46), nickel (0.000,012,65) and most metals.^{37a} This property of the alloy

corresponds to the formula CoO_2 . The reaction must be expressed by the equation: $\text{CoX}_2 + \text{I}_2 + 4\text{KHO} = \text{CoO}_2 + 2\text{KX} + 2\text{KI} + 2\text{H}_2\text{O}$.

³⁷ Prior to Vortmann, Rousseau (1889) endeavoured to solve the question as to whether CoO_2 was able to combine with bases and obtained $2(\text{CoO}_2)\text{BaO}$ and $\text{CoO}_2, \text{BaO} = \text{BaO}_2, \text{CoO}$, by breaking up the mass as it agglomerates together, and bringing the pieces into contact with the more heated surface of the crucible. This salt is formed between the somewhat narrow limits of temperature $1000^\circ\text{--}1100^\circ$; above and below these limits compounds richer or poorer in CoO_2 are formed. The formation of CoO_2 by the action of BaO_2 , and the easy decomposition of CoO_2 with the evolution of oxygen, give reason for thinking that it belongs to the class of peroxides (like Cr_2O_7 , CaO_2 , &c.); it is not yet known whether they give peroxide of hydrogen like the true peroxides. The fact that it is obtained by means of iodine (probably through HIO), coupled with its great resemblance to MnO_2 , leads rather to the supposition that CoO_2 is a very feeble saline oxide. The form CoO_2 is repeated in the cobaltic compounds (note 35), and the existence of CoO_2 should have long ago been recognised upon this basis.

^{37a} From a private communication I hear that Mons. Guillaume (September 1902) subsequently obtained the same 'invar' in such a state (whether by treatment or the addition of some substance to it, I do not know) that it does not expand when heated, but slightly contracts. All the above data hold good within the limits of 0° and 30° , but not for higher temperatures, when the structure of the metal and therefore the coefficient of expansion may vary.

approximating to NiFe_2 (it is called 'invar') renders it valuable for many scientific purposes, such as the preparation of standard measures of length, pendulums, &c., especially as it is very homogeneous, has a fine appearance, and is easily marked and polished. The alloys of Ni and Cu, containing a considerable proportion of Ni, are also silver white and just as suitable for making many scientific instruments, as they do not rust and take a very fine polish, which is essential for the inscription of micrometers, &c. In the arts, **german silver** is most extensively used; this is an alloy containing nickel, copper, and zinc in various proportions. It generally consists of about 50 per cent. of copper, 25 of zinc, and 25 of nickel. This alloy is white like silver, and does not rust, and therefore furnishes an excellent substitute for silver in the majority of cases where it is used. Alloys which contain silver in addition to nickel show the properties of silver to a still greater extent. Alloys of nickel are used for coinage, and if rich deposits of nickel are discovered a wide field of application lies before it, not only in a pure state (because it is a beautiful metal and does not rust), but also for use in alloys.^{37b}

Until 1890 no compound of cobalt or nickel was known of sufficient volatility to determine the molecular weights of the compounds of these metals; but in 1890 L. Mond, in conducting (together with Langer and Quincke) his researches on the action of nickel upon carbonic oxide (Chap. IX., note 24a), observed that nickel gradually volatilises in a stream of carbonic oxide; this only takes place at low temperatures, and is seen by the coloration of the flame of the carbonic oxide. This observation led to the discovery of a remarkable volatile compound of **nickel and carbonic oxide**, having the molecular composition $\text{Ni}(\text{CO})_4$,³⁸

^{37b} The salts of nickel are poisonous, like those of copper and silver, but like Ag, Ni oxidises with difficulty and does not form salts under ordinary conditions, while Cu forms salts with great ease.

³⁸ This compound is known as nickel tetra-carbonyl. It appears to me as yet premature to judge of the structure of such an extraordinary compound as $\text{Ni}(\text{CO})_4$. It has long been known that potassium combines with CO, forming $\text{K}_n(\text{CO})_n$ (Chap. IX., note 31), but this substance is apparently saline and non-volatile, and has as little in common with $\text{Ni}(\text{CO})_4$ as NaH has with SbH_3 . However, Berthelot observed that when NiC_4N_4 is kept in air, it oxidises, and gives a colourless compound, $\text{Ni}_3\text{C}_2\text{O}_3 \cdot 10\text{H}_2\text{O}$, having apparently saline properties. We may add that Schutzenberger, on reducing NiCl_2 by heating it in a current of hydrogen, observed that a nickel compound partly volatilises with the HCl and gives metallic nickel when heated again. The platinum compound, $\text{PtCl}_2(\text{CO})_2$ (Chap. XXIII., note 11), offers the greatest analogy to $\text{Ni}(\text{CO})_4$. This compound was obtained as a volatile substance by Schutzenberger (1868) by moderately heating (to 235°) metallic platinum in a mixture of chlorine and carbonic oxide. If we designate CO by Y, and an atom of chlorine by X, then, taking into account that, according to the periodic system, Ni is an analogue of Pt, a certain degree of correspondence is seen between the compositions NiY_4 and PtX_2Y_2 . It would be interesting to compare the reactions of the two compounds.

as determined by the vapour density and by the depression of freezing-point. Cobalt and many other metals do not form volatile compounds under these conditions, but iron gives a similar product (note 26a). $\text{Ni}(\text{CO})_4$ is prepared by taking finely divided Ni (obtained by reducing NiO by heating it in a stream of hydrogen, or by igniting the oxalate, NiC_2O_4)³⁹ and passing (at a temperature below 50° , for even at 60° decomposition may take place accompanied by an explosion) a stream of CO over it; the latter carries over the vapour of the compound, which condenses (in a well-cooled receiver) into a perfectly colourless, extremely mobile liquid, of sp. gr. 1.356 at 0° , boiling without decomposition at 43° , and crystallising in needles at -25° ; it is insoluble in water, but soluble in alcohol and benzene, and burns with a very smoky flame (due to the liberation of Ni). When passed through a tube heated to 180° and above, the vapour deposits a brilliant coating of metal, and disengages CO . If the tube is strongly heated the decomposition is accompanied by an explosion. If $\text{Ni}(\text{CO})_4$ as vapour is passed through a solution of CuCl_2 , it reduces the latter to metal; it has the same action upon an ammoniacal solution of AgCl . Strong nitric acid oxidises $\text{Ni}(\text{CO})_4$, but dilute solutions of acids have no action; if the vapour is passed through strong sulphuric acid, CO is liberated, while with chlorine it gives NiCl_2 and COCl_2 ; no simple reactions of double decomposition are yet known for $\text{Ni}(\text{CO})_4$, however, so that its connection with other carbon compounds is not clear.⁴⁰

³⁹ According to its empirical formula, anhydrous oxalate of nickel, NiC_2O_4 , contains nickel and 2CO_2 .

⁴⁰ The following are the thermo-chemical data (according to Thomsen, and referred to gram weights expressed by the formula, in large calories or thousands of heat units) for the formation of corresponding compounds of Mn, Fe, Co, Ni, and Cu (+ Aq signifies that the reaction proceeds in an excess of water):

	R = Mn	Fe	Co	Ni	Cu
$\text{R} + \text{Cl}_2 + \text{Aq}$	128	100	95	94	63
$\text{R} + \text{Br}_2 + \text{Aq}$	106	78	73	72	41
$\text{R} + \text{I}_2 + \text{Aq}$	76	48	43	41	32
$\text{R} + \text{O} + \text{H}_2\text{O}$	95	68	63	61	38
$\text{R} + \text{O}_2 + \text{SO}_2 + n\text{H}_2\text{O}$	193	169	163	163	130
$\text{RCl}_2 + \text{Aq}$	+ 16	18	18	19	11

These examples show that for analogous reactions the amount of heat evolved in passing from Mn to Fe, Co, Ni, and Cu varies in regular sequence as the atomic weight increases. A similar difference is to be found in other groups and series, and proves that thermo-chemical phenomena are subject to the periodic law. It is most remarkable that Co and Ni give almost the same quantities of heat and have almost the same atomic weights.

CHAPTER XXIII

THE PLATINUM METALS

THE six metals : ruthenium, Ru, rhodium, Rh, palladium, Pd, osmium, Os, iridium, Ir, and platinum, Pt, are met with in nature associated together. Platinum always predominates over the others, and hence they are known as the **platinum metals**. By their chemical character their position in the periodic system is in the eighth group, corresponding with iron, cobalt, and nickel.

The natural transition from titanium and vanadium to copper and zinc by means of the elements of the iron group is demonstrated by all the properties of these elements, and in exactly the same manner a transition from zirconium, niobium, and molybdenum to silver, cadmium, and indium, through ruthenium, rhodium, and palladium, is in perfect accordance with their properties and with the magnitude of the atomic weights, as also is the position of osmium, iridium, and platinum between tantalum and tungsten on the one side, and gold and mercury on the other. In all these three cases the elements of smaller atomic weight (chromium, molybdenum, and tungsten) are able, in their higher grades of oxidation, to give acid oxides having the properties of distinct but feebly energetic acids (in the lower oxides they give bases), whilst the elements of greater atomic weight (zinc, cadmium, mercury), even in their higher grades of oxidation, only give bases, and then only rather feeble ones. The platinum metals in forming comparatively feeble oxides with oxygen present the same intermediate properties as we have already seen in iron and the elements of the eighth group.

In the platinum metals the intermediate properties of **feebly acid and feebly basic metals** are developed with great clearness, so that there is not one sharply defined acid anhydride among their oxides, although there is a great diversity in the grades of oxidation, varying from the type RO_4 to R_2O . The feebleness of the chemical forces observed in the platinum metals is connected with the ready decomposability of their compounds. The oxides of platinum, iridium, and osmium can scarcely be termed either basic or acid; they are capable of combinations of both kinds, each of which is feeble, i.e., they are intermediate oxides.

The atomic weights of platinum, iridium, and osmium are about 191 to 196, and those of palladium, rhodium, and ruthenium, 104 to 106. Thus, strictly speaking, we have here two series of metals, which are, moreover, perfectly parallel to each other; three members in the first series, and three members in the second—platinum presents an analogy to palladium, iridium to rhodium, and osmium to ruthenium. As a matter of fact, however, the whole **group** of the platinum metals is characterised by **a number of common properties**, both physical and chemical, and, moreover, there are several points of resemblance between the members of this group and those of the **iron** group (Chap. XXII.). The atomic volumes of the elements of this group are **nearly equal** and **very small**. The iron metals have atomic volumes of about 7, whilst that of the metals allied to palladium is nearly 9, and of those adjacent to platinum (Pt, Ir, Os), nearly 9·4. This comparatively small atomic volume corresponds with the great infusibility and tenacity peculiar to all the iron and platinum metals, and to their small chemical energy, which stands out very clearly in the heavy platinum metals. All the platinum metals are very **easily reduced** by ignition and by the action of various reducing agents, in which process oxygen, or a haloid group, is disengaged from their compounds and the metal left behind. This is a property of the platinum metals which determines many of their reactions, and the circumstance of their always being found in nature **in a native state**. In Russia, in the Urals (discovered in 1819), and in Brazil (1735), platinum is obtained from alluvial deposits; but in 1892 Professor Inostrantseff discovered a vein deposit of platinum in serpentine near Tagil in the Urals.¹ Now almost all the platinum produced (about 6 tons a year) comes from the Urals.

The facility with which the platinum metals are reduced is so great that their chlorides are even decomposed by gaseous hydrogen, especially when shaken up and heated under a certain pressure. Hence it will be readily understood that such metals as zinc, iron, &c., separate them from solutions with great ease, this fact being taken advantage of in practice and in the chemical treatment of the platinum metals.^{1a}

¹ Wells and Penfield (1888) have described a mineral, sperrylite, found in the Canadian gold-bearing quartz and consisting of platinum diarsenide, PtAs_2 . It is a noticeable fact that this mineral clearly confirms the position of platinum in the same group as iron, because it corresponds in crystalline form (dodecahedra of the regular system) and chemical composition with iron pyrites, FeS_2 .

^{1a} Some light is thrown upon the facility with which the platinum compounds decompose, by Thomsen's data, which show that in an excess of water (+ Aq) the formation from platinum of such a double salt as $\text{PtCl}_2 \cdot 2\text{KCl}$, is accompanied by a comparatively small evolution of heat (see Chap. XXI., note 40), for instance, $\text{Pt} + \text{Cl}_2 + 2\text{KCl} + \text{Aq}$ only

All the platinum metals are grey, with a comparatively feeble metallic lustre, and are very infusible. In this respect they stand in the same order as the metals of the iron series; nickel is more fusible and whiter than cobalt and iron, and so also palladium is whiter and more fusible than rhodium and ruthenium, and platinum comparatively more fusible and whiter than iridium or osmium. The saline compounds of these metals are red or yellow. Moreover, certain complex compounds of the platinum metals, like certain complex compounds of the iron series, either have particular characteristic tints or are else colourless.

The platinum metals are found in nature associated together in the **alluvial deposits** of a few localities, from which they are washed, owing to their very considerable density, which enables a stream of water to remove the sand and clay with which they are mixed. Platinum deposits are known chiefly in the Urals, and also in Brazil and a few other localities. The platinum ore washed from these alluvial deposits presents the appearance of more or less coarse grains, and sometimes, as it were, of semi-fused nuggets.²

All the platinum metals give compounds with the halogens, and the highest haloid type of combination for all is RX_4 . For the majority of the platinum metals this type is exceedingly unstable; the lower compounds, corresponding to the type RX_2 , are more stable. In this type, RX_2 , the platinum metals offer no little resemblance to the kindred compounds of the iron series—for example, to nickelous chloride, $NiCl_2$, cobaltous chloride, $CoCl_2$, &c. This even expresses itself in a similarity of volume (platinous chloride, $PtCl_2$, volume, 46; nickelous chloride, $NiCl_2$, 50), although in the type RX_2 the true iron metals give very stable compounds, whilst the platinum metals frequently react after the manner of suboxides, decomposing into the metal and higher types,

evolves about 33,000 calories (hence the reaction, $Pt + Cl_2 + Aq$, will evidently disengage still less, because $PtCl_2 + 2KCl$ evolves a certain amount of heat), whilst on the other hand, $Fe + Cl_2 + Aq$ gives 100,000 calories, and even the reaction with copper (for the formation of the double salt) evolves 63,000 calories.

² In the Urals a certain amount of gold is extracted from the washed platinum by means of mercury, which does not dissolve the platinum metals but dissolves the gold accompanying the platinum in its ores. The washed and mechanically sorted ore, in the majority of cases, contains about 70 to 80 per cent. of platinum, about 5 to 8 per cent. of iridium, and a somewhat smaller quantity of osmium. The other platinum metals—palladium, rhodium, and ruthenium—occur in smaller proportions than the above-named. Sometimes grains of almost pure osmium-iridium, containing only a small quantity of other metals, are found in platinum ores. This **osmium-iridium** may be easily separated from the other platinum metals, owing to its being nearly insoluble in aqua regia, by which the latter are easily dissolved. There are grains of platinum which are magnetic. The grains of osmium-iridium are very hard and malleable, and are therefore used for certain purposes, for instance, for the tips of fountain pens.

$2RX_2 = R + RX_4$. This probably depends on the facility with which RX_2 decomposes into R and X_2 , the latter then combining with the remaining portion of RX_2 .

As in the series iron, cobalt, and nickel, nickel gives NiO and Ni_2O_3 , whilst cobalt and iron give higher and varied forms of oxidation, so also among the platinum metals, platinum and palladium only give the forms RX_2 and RX_4 , whilst rhodium and iridium form another and intermediate type, RX_3 , also met with in cobalt, corresponding with the oxide having the composition R_2O_3 , besides which they form an acid oxide, like ferric acid, which is also known in the form of salts, but is in every respect unstable. **Osmium** and **ruthenium**, like manganese, form still higher oxides, and in this respect exhibit the greatest diversity. They not only give RX_2 , RX_3 , RX_4 , and RO_2X_2 , but also a still **higher form of oxidation**, RO_4 , which is not met with in any other series. This form is exceedingly characteristic, owing to the fact that the oxides, OsO_4 and RuO_4 , are volatile and have feebly acid properties. In this respect they most resemble permanganic anhydride, which is also somewhat volatile.³

When dissolved in aqua regia ($PtCl_4$ is formed) and liberated from the solution by sal-ammoniac [$(NH_4)_2PtCl_6$ is formed] and reduced by ignition (which may be done by Zn and other reducing agents, directly from a solution of $PtCl_4$) platinum ^{3a} forms a powdery mass, known

³ The platinum metals are capable of forming a sort of unstable compound with **hydrogen**; they absorb the gas and only part with it when somewhat strongly heated. This faculty is especially developed in platinum and palladium, and it is very characteristic that nickel, which exactly corresponds with platinum and palladium in the periodic system, should exhibit the same faculty for retaining a considerable quantity of hydrogen (Graham's and Raoult's experiments). Another characteristic property of the platinum metals consists in their easily giving (like cobalt, which forms the cobaltic salts) complex saline **compounds with ammonia**, and, like Fe and Co , double salts with the cyanides of the alkali metals, especially in their lower forms of combination.

^{3a} Platinum was first obtained in the eighteenth century from Brazil, where it was called silver (*platinas*). Watson characterised platinum as a separate independent metal. In 1803 Wollaston discovered palladium and rhodium in crude platinum, and at about the same time Tennant distinguished iridium and osmium in it. Professor Claus, of Kazan, in his researches on the platinum metals (about 1840) discovered ruthenium in them, and to him are due many important discoveries with regard to these elements, including the indication of the remarkable analogy between the series $Pd-Rh-Ru$ and $Pt-Ir-Os$.

The treatment of platinum ore is chiefly carried on for the extraction of the platinum itself and of its alloys with iridium, because these metals offer a greater resistance to the action of chemical reagents and high temperatures than any of the other malleable and ductile metals, and therefore the wire so often used in the laboratory and for technical purposes (especially in electro-technics) is made from them, as also are various vessels used for chemical purposes in the laboratory and in works. Thus sulphuric acid is distilled in platinum retorts, and many substances are fused, ignited, and evaporated in the laboratory in platinum crucibles and on platinum foil. Gold, &c., are

as spongy platinum or platinum black. If this powder of platinum is heated and pressed, or hammered in a cylinder, the grains aggregate or forge together, and form a continuous, though not entirely homogeneous, mass. Platinum was formerly worked up in this manner. The platinum money formerly used in Russia was made in this way. Sainte-Claire Deville, in the fifties, for the first time melted platinum in considerable quantities by employing a special furnace made in the form of a small reverberatory furnace, and composed of two pieces of lime, on which the heat of the oxyhydrogen flame has no action. Into this furnace (shown in fig. 38, Vol. I., p. 172)—or, more strictly speaking, into the cavity made in the pieces of lime—the platinum is introduced, and two orifices are made in the lime; through one, the upper, or side orifice, is introduced an oxyhydrogen gas burner, in which either detonating gas or a mixture of oxygen and coal-gas is burnt, whilst the other orifice serves for the escape of the products of combustion and certain impurities which are more volatile than the platinum, and especially the oxidised compounds of osmium, ruthenium (and palladium), which are comparatively easily volatilised by heat. In this manner the platinum is converted into a homogeneous metallic form by means of fusion.⁴

To obtain pure platinum, the ore is treated with aqua regia in which only the osmium and iridium are insoluble. The solution contains the platinum metals in the form RCl_4 , and in the lower forms of chlorina-

dissolved in dishes made of iridium-platinum, because the alloys of platinum and iridium are but slightly attacked when subjected to the action of aqua regia.

The comparatively high density (about 21.5), hardness—nearly that of steel (Pt is soft)—ductility, and infusibility (it does not melt at a furnace heat, but only in the oxyhydrogen flame or electric furnace), as well as the fact of its resisting the action of water, air, and other reagents, renders an alloy of 90 parts of platinum and 10 parts of iridium (Deville's platinum-iridium alloy) a most valuable material for making standard weights and measures, such as the metre, kilogram, and pound, and therefore all the newest standards of most countries are made of this alloy.

⁴ This process has altered the technical treatment of platinum to a considerable extent. It has in particular facilitated the manufacture of alloys of platinum with iridium and rhodium from the pure platinum ores, since it is sufficient to fuse the ore in order for the greater amount of the osmium to burn off, and for the mass to fuse into a homogeneous malleable alloy, which can be directly made use of. There is very little ruthenium in the ores of platinum. If during fusion lead is added, it dissolves the platinum (and other platinum metals), owing to its being able to form a very characteristic alloy of the composition PtPb . If an alloy of the two metals is left exposed to moist air, the excess of lead is converted into carbonate (white lead) in the presence of the water and carbonic acid of the air, whilst the above platinum alloy remains unchanged. The white lead may be extracted by dilute acid, and the alloy PtPb remains unaltered. The fusibility of these alloys enables the platinum metals to be separated from the gangue of the ore, and they may afterwards be separated from the lead by subjecting the alloy to oxidation in furnaces furnished with a bone ash bed, because the lead is then oxidised and absorbed by the bone ash, leaving the platinum metals untouched (H. Sainte-Claire Deville, 1865).

tion, RCl_3 and RCl_2 , because some of these metals—for instance, palladium and rhodium—form such unstable chlorides of the type RX_4 that they partially decompose even when diluted with water, and pass into the stable lower type of combination ; in addition to which, the chlorine is very easily disengaged if it comes into contact with substances on which it can act. In this respect platinum resists the action of heat and reducing agents better than any of its companions—that is, it passes with greater difficulty from $PtCl_4$ to the lower compound $PtCl_2$. On this is based the method of preparation of more or less pure platinum. Lime or sodium hydroxide is added to the solution in aqua regia until the liquid is neutralised or only contains a very slight excess of alkali. It is best to first evaporate and slightly ignite the solution, in order to remove the excess of acid, and by heating it to partially convert the higher chlorides of the palladium, &c., into the lower. The addition of alkalies completes the reduction, because the chlorine held in the compounds RX_4 acts on the alkali like free chlorine, converting it into a hypochlorite. Thus palladium chloride, $PdCl_4$, for example, is converted into palladous chloride, $PdCl_2$, by this means, according to the equation, $PdCl_4 + 2NaHO = PdCl_2 + NaCl + NaClO + H_2O$. In a similar manner iridic chloride, $IrCl_4$, is converted into the trichloride, $IrCl_3$, by this method. When this conversion takes place, the platinum still remains in the form of platinic chloride, $PtCl_4$. It is then possible to take advantage of a certain difference in the properties of the higher and lower chlorides of the platinum metals. Thus lime precipitates the lower chlorides of the members of the platinum metals occurring in solution without acting on the platinic chloride, $PtCl_4$, and hence the addition of a large proportion of lime immediately precipitates the associated metals, leaving the platinum itself in solution in the form of a soluble double salt, $PtCl_4, CaCl_2$. A far better and more perfect separation is effected by means of ammonium chloride, which gives, with platinic chloride, an insoluble yellow precipitate, $PtCl_4, 2NH_4Cl$, whilst it forms soluble double salts with the lower chlorides RCl_2 and RCl_3 , so that ammonium chloride precipitates the platinum only from the solution obtained by the preceding method. These methods are employed for preparing the platinum which is used for the manufacture of platinum articles, because, having platinum in solution as calcium platinichloride, $PtCaCl_6$, or as the insoluble ammonium platinichloride, $Pt(NH_4)_2Cl_6$, the platinum compound in every case, after drying or ignition, loses all the chlorine from the platinic chloride and leaves finely divided metallic platinum, which may be converted into homogeneous metal by compression and forging, or by fusion.⁵

⁵ For the ultimate purification of platinum from palladium and iridium the metals

Metallic platinum in a fused state has a specific gravity of about 21; it is grey, softer than iron, but harder than copper, exceedingly ductile, and therefore easily drawn into wire and rolled into thin sheets, and may be hammered into crucibles and drawn into thin tubes, &c. In the state in which it is obtained by the ignition of its compounds, it forms a spongy mass, known as spongy platinum, or else as powder

must be re-dissolved in aqua regia, and the solution evaporated until the residue begins to evolve chlorine. The residue is then re-precipitated with ammonium or potassium chloride. The precipitate may still contain a certain amount of iridium, which passes with greater difficulty from the tetrachloride, IrCl_4 , into the trichloride, IrCl_3 ; but it will be quite free from palladium, because the latter easily loses its chlorine and passes into palladious chloride, PdCl_2 , which gives an easily soluble salt with potassium chloride. The precipitate, containing a small quantity of iridium, is then heated with sodium carbonate, giving metallic platinum and iridium oxide. If potassium chloride has been employed, the residue after ignition is washed with water and treated with aqua regia. The iridium oxide remains undissolved, and the platinum passes easily into solution. Only cold and dilute aqua regia must be used. The solution will then contain pure platinic chloride, which forms the starting-point for the preparation of all platinum compounds. The three following are very sensitive tests (to thousandths of a per cent.) for the presence of Ir, Ru, Rh, Pd (osmium is not usually present in platinum which has once been purified, since it easily volatilises with Cl_2 and CO_2 , and in the first treatment of the crude platinum either passes off as OsO_4 or remains undissolved), Fe, Cu, Ag, and Pb: (1) the assay is alloyed with 10 parts of pure lead, the alloy treated with dilute nitric acid (to remove the greater part of the Pb), and dissolved in aqua regia; the residue will consist of Ir and Ru; the Pb is precipitated from the nitric acid solution by sulphuric acid, whilst the remaining platinum metals are reduced from the evaporated solution by formic acid, and the resultant precipitate fused with KHSO_4 ; the Pd and Rh are thus converted into soluble salts, and the former is then precipitated by HgC_2N_2 . (2) Iron may be detected by the usual reagents, if the crude platinum be dissolved in aqua regia, and the platinum metals precipitated from the solution by formic acid. (3) If crude platinum (as foil or sponge) is heated in a mixture of chlorine and carbonic oxide, it volatilises (with a certain amount of Ir, Pd, Fe, &c.) as $\text{PtCl}_2 \cdot 2\text{CO}$ (note 11), whilst the whole of the Rh, Ag, and Cu it may contain remains behind. Among other characteristic reactions for the platinum metals, we may mention: (1) that rhodium is precipitated from the solution obtained after fusion with KHSO_4 (in which Pt does not dissolve) by NH_3 , acetic and formic acids; (2) that dilute aqua regia dissolves precipitated Pt, but not Rh; (3) that if the insoluble residue of the platinum metals (Ir, Ru, Os) obtained, after treating with aqua regia, be fused with a mixture of 1 part of KNO_3 and 3 parts of K_2CO_3 (in a gold crucible), and then treated with water, it gives a solution containing the Ru (and a portion of the Ir), but which throws it all down when saturated with chlorine and boiled; (4) that if iridium is fused with a mixture of KHO and KNO_3 , it gives a soluble potassium salt, IrK_2O_4 (the solution is blue), and this, when saturated with chlorine, gives IrCl_4 , which is precipitated by NH_4Cl (the precipitate is black), forming a double salt, leaving metallic Ir after ignition; (5) that rhodium mixed with NaCl and ignited in a current of chlorine gives a soluble double salt (from which sal-ammoniac separates Pt and Ir), which gives (according to Jürgensen) a difficultly soluble purpureo-salt (Chap. XXII., note 35), $\text{Rh}_2\text{Cl}_3 \cdot 5\text{NH}_3$, when treated with NH_3 ; in this form the Rh may be easily purified and obtained as metal by igniting in hydrogen; and (6) that palladium, dissolved in aqua regia and dried (NH_4Cl throws down any Pt), gives soluble PdCl_2 , which forms an easily crystallisable yellow salt, $\text{PdCl}_2 \cdot \text{NH}_3$, with ammonia; this salt (Wilm) may be easily purified by crystallisation, and gives metallic Pd when ignited. These reactions illustrate the method of separating the platinum metals from each other.

(platinum black).⁶ In either case it is dull-grey, and is characterised, as we already know, by the faculty of absorbing hydrogen and other gases. Platinum is not acted on by hydrochloric, hydriodic, nitric, and sulphuric acids, or by a mixture of hydrofluoric and nitric acids. Aqua regia, or any liquid containing chlorine or able to evolve chlorine or bromine, dissolves platinum. Alkalies are decomposed by platinum at a red heat, owing to the faculty of the platinum oxide, PtO_2 , formed to combine with alkaline bases, inasmuch as it has a feebly developed acid character (see note 8). Sulphur, phosphorus (the phosphide, PtP_2 , is formed), arsenic, silicon, and especially antimony, all act more or less rapidly on platinum, under the influence of heat. Many of the metals form alloys with it. Even charcoal combines with platinum when it is ignited with it, and therefore carbonaceous matter cannot be subjected to prolonged and powerful ignition in platinum vessels. Hence a platinum crucible soon becomes dull on the surface in a smoky flame. Platinum also forms alloys with zinc, lead, tin, antimony, copper, gold, and silver.⁷ Although mercury does not directly dissolve platinum, still it forms a solution or amalgam with spongy platinum in the presence of sodium amalgam; a similar amalgam is also formed by the action of sodium amalgam on a solution of platinum chloride, and is used for physical experiments.

There are **two kinds of platinum compounds**, PtX_4 and PtX_2 . The former are produced by an excess of halogen in the cold, and the

⁶ We have already become acquainted with the effect of finely divided platinum on many gaseous substances. It is best seen in the so-called **platinum black**, which is a grey or black powder, left by the action of sulphuric acid on the alloy of zinc and platinum, or precipitated by metallic zinc from a dilute solution of platinum. In any case, finely divided platinum absorbs gases more powerfully and rapidly the more finely divided and porous it is. Sulphurous anhydride, hydrogen, alcohol, and many organic substances in the presence of such platinum are easily oxidised by the oxygen of the air, although they do not combine with it directly. The absorption of oxygen is as much as several hundred volumes per one of platinum, and the oxidising power of such absorbed oxygen is taken advantage of not only in the laboratory, but even in manufacturing processes. Asbestos or charcoal, soaked in a solution of platinic chloride and ignited, is very useful for this purpose, because by this means it becomes coated with platinum black (Chap. XX., note 48a). If 50 grams of PtCl_4 is dissolved in 60 c.c. of water, and 70 c.c. of a strong (40 p.c.) solution of formic aldehyde added, the mixture cooled, and then a solution of 50 grams of NaHO in 50 grams of water added, the platinum is precipitated. After washing with water the precipitate passes into solution and forms a black liquid containing *soluble colloidal platinum* (Loew, 1890). If the precipitated platinum be allowed to absorb oxygen on the filter, the temperature rises 40° , and a very porous *platinum black* is obtained which vigorously facilitates oxidation.

⁷ It is necessary to remark that platinum when alloyed with silver, or as amalgam, is soluble in nitric acid, and in this respect it differs from gold, so that it is possible, by alloying gold with silver, and acting on the alloy with nitric acid, to recognise the presence of platinum in the gold, because nitric acid does not act on gold alloyed with silver.

latter by the aid of heat or by the splitting up of the former. The starting-point for the platinum compounds is **platinum tetrachloride**, or **platinic chloride**, PtCl_4 , obtained by dissolving platinum in aqua regia.^{7a} The solution crystallises in the cold, in a desiccator, in the form of reddish-brown deliquescent crystals which contain hydrochloric acid, $\text{PtCl}_4 \cdot 2\text{HCl} \cdot 6\text{H}_2\text{O}$, and behave like a true acid whose salts correspond to the formula R_2PtCl_6 —ammonium platinichloride, for example.^{7b} The hydrochloric acid is liberated from the HCl compound by gently heating (or, better still, after treatment with silver nitrate), a reddish-brown mass remaining behind, yielding a yellowish-red solution which on cooling deposits crystals of the composition $\text{PtCl}_4 \cdot 8\text{H}_2\text{O}$. The **tendency of PtCl_4 to combine with hydrochloric acid and water—that is, to form higher crystalline compounds**—is evident in all the platinum compounds, and must be taken into account in explaining the formation of many others of its complex compounds. Dilute solutions of platinic chloride are yellow, and are completely reduced by hydrogen, sulphurous anhydride, and many reducing agents, which first convert the platinic chloride into the lower compound, platinous chloride, PtCl_2 . That faculty, which reveals itself in platinum tetrachloride, of combining with water of crystallisation and hydrochloric acid, is distinctly marked in its property, with which we are already acquainted, of giving precipitates with the salts of potassium, ammonium, rubidium, &c. In general it **readily forms double salts**, $\text{R}_2\text{PtCl}_6 = \text{PtCl}_4 + 2\text{RCl}$, where R is a univalent metal such as potassium or NH_4 . Hence the addition of a solution of potassium or ammonium chloride to a solution of platinic chloride is followed by the formation of a yellow precipitate, which is sparingly soluble in water and almost entirely insoluble in alcohol and ether (platinic chloride is soluble in alcohol, potassium iridichloride, IrK_3Cl_6 , i.e., a compound of IrCl_2 , being soluble in water but not in alcohol). It is especially remarkable in this case that here, as in many other instances, the potassium compounds separate in an anhydrous form, whilst the sodium compounds, which are soluble in water and alcohol, form red crystals containing water. The composition $\text{Na}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ exactly corresponds with the above-mentioned hydrochloric compound. The compounds

^{7a} PtCl_4 is also formed by the action of a mixture of HCl vapour and air, and by the action of gaseous chlorine, upon platinum.

^{7b} Pigeon (1891) obtained fine yellow crystals of $\text{PtH}_2\text{Cl}_6 \cdot 4\text{H}_2\text{O}$ by adding strong sulphuric acid to a strong solution of $\text{PtH}_2\text{Cl}_6 \cdot 6\text{H}_2\text{O}$. If crystals of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ are melted *in vacuo* (60°) in the presence of anhydrous potash, a red-brown solid hydrate is obtained containing less water and HCl , which parts with the remainder at 200° , leaving anhydrous PtCl_4 . The latter does not disengage chlorine before 220° , and is perfectly soluble in water.

with barium, $\text{BaPtCl}_6, 4\text{H}_2\text{O}$, strontium, $\text{SrPtCl}_6, 8\text{H}_2\text{O}$, calcium, magnesium, iron, manganese, and many other metals are all soluble in water.⁸

Platinous chloride, PtCl_2 , is formed when hydrogen platinichloride, PtH_2Cl_6 , is ignited at 300° , or when platinum is heated at 230° in a stream of chlorine. The undecomposed tetrachloride is extracted from the residue by washing it with water, and a greenish-grey or brown insoluble mass of the dichloride (sp. gr. 5.9) is then obtained. It is soluble in hydrochloric acid, giving an acid solution of the composition $\text{PtCl}_2, 2\text{HCl}$, corresponding with the type of double salts, PtR_2Cl_4 . Although platinous chloride decomposes below 500° , it is still formed to a small extent at higher temperatures. Troost and Hautefeuille, and Seelheim observed that when platinum was strongly ignited in a stream of chlorine, the metal, as it were, slowly volatilised and was deposited in crystals; a volatile chloride, probably platinous chloride, was evidently formed in this case, and decomposed subsequently to its formation, depositing crystals of platinum.

The above-described properties of platinum are repeated more or less distinctly, or sometimes with certain modifications in the above-mentioned associates and analogues of this metal. Thus, although palladium

⁸ Nilson (1877), who investigated the platinochlorides of various metals subsequently to Bonsdorff, Topsøe, Clève, Marignac, and others, found that univalent and bivalent metals—such as hydrogen, potassium, ammonium . . . beryllium, calcium, barium—give compounds of such a composition that there is always twice as much chlorine in the platinic chloride as in the combined metallic chloride; for example, $\text{K}_2\text{Cl}_2, \text{PtCl}_4$; $\text{BaCl}_2, \text{PtCl}_4, 8\text{H}_2\text{O}$, &c. Such trivalent metals as aluminium, iron (ferric), chromium, didymium, and cerium (cerous) form compounds of the type $\text{RCl}_3, \text{PtCl}_4$, in which the amounts of chlorine are in the ratio 3 : 4. Only indium and yttrium give salts of a different composition—namely, $2\text{InCl}_3, 5\text{PtCl}_4, 36\text{H}_2\text{O}$ and $4\text{YCl}_3, 5\text{PtCl}_4, 51\text{H}_2\text{O}$. Such quadrivalent metals as thorium, tin, and zirconium give compounds of the type $\text{RCl}_4, \text{PtCl}_4$, in which the ratio of the chlorine is 1 : 1. In this manner the valency of a metal may, to a certain extent, be judged from the composition of the double salts formed with platinic chloride.

Platinic bromide, PtBr_4 , and iodide, PtI_4 , are analogous to the tetrachloride, but the iodide is decomposed still more easily than the chloride. If sulphuric acid is added to platinic chloride, and the solution evaporated, it forms a black porous mass like charcoal, which deliquesces in the air, and has the composition $\text{Pt}(\text{SO}_4)_2$. But this, the only oxygen salt of the type PtX_4 , is exceedingly unstable. This is due to the fact that **platinum oxide**, the oxide of the type PtO_2 , has a feeble acid character. This is shown in a number of instances. Thus, if a strong solution of platinic chloride treated with sodium carbonate be exposed to the action of light or evaporated to dryness and then washed with water, a sodium platinate, $\text{Pt}_3\text{Na}_2\text{O}_7, 6\text{H}_2\text{O}$, remains. The composition of this salt, if we regard it in the same sense as we did the salts of silicic, titanio, molybdic, and other acids, will be $\text{PtO}(\text{ONa})_3, 2\text{PtO}_2, 6\text{H}_2\text{O}$ —that is, the same type is repeated as we saw in the crystalline compounds of platinum tetrachloride with sodium chloride, or with hydrochloric acid—namely, the type $\text{PtX}_4, 8\text{Y}$, where Y is a molecule of H_2O , HCl , &c. Similar compounds are also obtained with other alkalies. They will be platinales of the alkalies in which the platinic oxide, PtO_2 , plays the part of an acid oxide. Rousseau (1889) obtained different grades of combination $\text{BaO}, \text{PtO}_2, 3(\text{BaO}), 2\text{PtO}_2$, &c., by igniting a mixture of PtCl_4 and caustic baryta. If such an alkaline compound of platinum is

forms PdCl_4 , this form passes into PdCl_2 with extreme ease.⁹ Whilst rhodium and iridium in dissolving in aqua regia also form RhCl_4 and

treated with acetic acid, the alkali combines with the latter, and a **platinic hydroxide**, $\text{Pt}(\text{OH})_4$, remains as a brown mass, which loses water and oxygen when ignited, and in so doing decomposes with a slight explosion. When slightly ignited this hydroxide first loses water and gives the very unstable oxide, PtO_2 . Platinic sulphide, PtS_2 , belongs to the same type; it is precipitated by the action of sulphuretted hydrogen on a solution of platinum tetrachloride. The moist precipitate is capable of attracting oxygen, and is then converted into the sulphate above mentioned, which is soluble in water. This absorption of oxygen and conversion into sulphate is another illustration of the basic nature of PtO_2 , so that it clearly exhibits both basic and acid properties. The latter appear, for instance, in the fact that platinic sulphide, PtS_2 , gives crystalline compounds with the alkali sulphides.

⁹ In comparing the characteristics of the platinum metals, it must be observed that palladium, in its form of combination PdX_2 , gives saline compounds of considerable stability. Amongst them **palladous chloride** is formed by the direct action of chlorine or aqua regia (not in excess or in dilute solutions) on palladium. It forms a brown solution, which gives a black insoluble precipitate of **palladous iodide**, PdI_2 , with solutions of iodides (in this respect, as in many others, palladium resembles mercury in the mercuric compounds, HgX_2). With a solution of mercuric cyanide it gives a yellowish-white precipitate, palladous cyanide, PdC_2N_2 , which is soluble in potassium cyanide, and gives other double salts, $\text{M}_2\text{PdC}_2\text{N}_4$.

That portion of the platinum ore which dissolves in aqua regia and is precipitated by ammonium or potassium chloride does not contain palladium. It remains in solution, because the palladic chloride, PdCl_4 , is decomposed and the palladous chloride formed is not precipitated by ammonium chloride; the same holds good for all the other lower chlorides of the platinum metals. Zinc (or iron) separates out all the unprecipitated platinum metals (and also copper, &c.) from the solution. The palladium is found in these 'platinum residues' precipitated by zinc. If this mixture of metals be treated with aqua regia, all the palladium will pass into solution as palladous chloride, together with some platinic chloride. By this treatment the main portion of the iridium, rhodium, &c., remains almost undissolved, the platinum is separated from the mixture of palladous and platinic chlorides by a solution of ammonium chloride, and the solution of palladium is precipitated by potassium iodide or mercuric cyanide. Wilm (1881) showed that palladium may be separated from an impure solution by saturating it with ammonia; all the iron present is thus precipitated, and, after filtering, the addition of hydrochloric acid to the filtrate gives a yellow precipitate of an ammonio-palladium compound, $\text{PdCl}_2 \cdot 2\text{NH}_3$, whilst nearly all the other metals remain in solution. **Metallic palladium** is obtained by igniting the ammonio-compound or the cyanide, PdC_2N_2 . It occurs native, although rarely, is a metal of a whiter colour than platinum, has the sp. gr. 11.4, and melts at about 1500° ; it is much more volatile than platinum, and partially oxidises on the surface when heated. Wilm obtained spongy palladium by igniting $\text{PdCl}_2 \cdot 2\text{NH}_3$, and observed that it gives PdO (together with Pd_2O , according to Ramsay) when ignited in oxygen, and that on further ignition this oxide forms a mixture of Pd_2O and Pd and loses its absorbed oxygen on a further rise of temperature. It does not blacken or tarnish (does not absorb sulphur) in the air at the ordinary temperature, and is therefore better suited than silver for astronomical and other instruments in which fine divisions have to be engraved on a white metal, in order that the fine lines should be clearly visible. The most remarkable property of palladium, discovered by Graham, consists in its capacity for **absorbing** a large amount of **hydrogen**. Ignited palladium absorbs as much as 940 volumes of hydrogen, or about 0.7 per cent. of its own weight, which closely approaches to the formation of the compound Pd_3H_2 , and probably indicates the formation of **palladium hydride**, Pd_2H . This absorption also takes place at the ordinary temperature—for example, when palladium serves as an electrode at which hydrogen is evolved. In absorbing the hydrogen, the palladium does not change

IrCl_4 , but these pass into RhCl_3 and IrCl_3 ^{9a} very easily when heated or when acted upon by substances capable of taking up chlorine (even

in appearance, and retains all its metallic properties, but its volume increases about 10 per cent.—that is, the hydrogen pushes out and separates the atoms of the palladium from each other, and is itself compressed to $\frac{1}{100}$ of its volume. This compression indicates a great force of chemical attraction, and is accompanied by the evolution of heat (Chap. II., note 38). The absorption of 1 gm. of hydrogen by metallic palladium (Favre) is accompanied by the evolution of 4.2 thousand calories (for Pt, 20; for Na, 13; for K, 10 thousand units of heat). Troost showed that the dissociation pressure of palladium hydride is inconsiderable at the ordinary temperature, but reaches the atmospheric pressure at about 140°. All the hydrogen passes off at 440°. This subject was subsequently investigated by A. A. Cracow (1894), who showed that at first the absorption of hydrogen by the palladium proceeds like solution, according to the law of Daltou and Henry, but that towards the end it proceeds like a dissociation phenomenon in definite compounds; this forms another link between the phenomenon of solution and that of the formation of definite atomic compounds.

The absorbed hydrogen is easily disengaged by ignition or decreased pressure. The resultant compound does not decompose at the ordinary temperature, but when exposed to air the metal sometimes glows spontaneously, owing to the hydrogen burning at the expense of the atmospheric oxygen. The hydrogen absorbed by palladium acts towards many solutions as a reducing agent; in a word, everything here points to the formation of a definite compound and at the same time of a physically compressed gas, and forms one of the best examples of the bond existing between chemical and physical processes, to which we have many times drawn attention. It must be again remembered that the other metals of the eighth group, even copper, are, like palladium and platinum, able to combine with hydrogen. The permeability of iron and platinum tubes to hydrogen is naturally due to the formation of similar compounds, but palladium is the most permeable.

^{9a} **Rhodium** is generally separated, together with iridium, from the residues left after the treatment of native platinum (note 9), because the palladium is entirely separated from them, and the ruthenium is present in them in very small traces, whilst the osmium at any rate is easily separated, as we shall soon see. The mixture of rhodium and iridium which is left undissolved in dilute aqua regia is dissolved in chlorine water, or by the action of chlorine on a mixture of the metals with sodium chloride. In either case both metals pass into solution. They may be separated by many methods. The rhodium is obtained (if the action be aided by heat) in the form of the chloride RhCl_3 , and the iridium as iridic chloride, IrCl_3 . With sodium chloride they both form double salts, which are soluble in water, but the iridium salt is also partially soluble in alcohol, whilst the rhodium salt is not. A mixture of the chlorides, when treated with dilute aqua regia, gives iridic chloride, IrCl_4 , whilst the rhodium chloride, RhCl_3 , remains unaltered; ammonium chloride then precipitates the iridium as ammonium iridichloride, $\text{Ir}(\text{NH}_4)_2\text{Cl}_6$, and on evaporating the rose-coloured filtrate the rhodium gives a crystalline salt, $\text{Rh}(\text{NH}_4)_3\text{Cl}_6$. Rhodium and its various oxides are dissolved when fused with potassium hydrogen sulphate, and give a soluble double sulphate (whilst iridium remains unacted on); this fact is very characteristic for this metal, which offers in its properties many points of resemblance with the iron metals. When fused with potassium hydroxide and chlorate it is oxidised like iridium, but it is not afterwards soluble in water, in which respect it differs from ruthenium. This is taken advantage of for separating rhodium, ruthenium, and iridium. In any case, rhodium under ordinary conditions always gives salts of the type RX_3 , and not of any other type; and not only halogen salts, but also oxygen salts, are known in this type, which is rare among the platinum metals. Rhodium chloride, RhCl_3 , is known in an insoluble anhydrous, and also in a soluble, form (like CrX_3 or salts of chromic oxides), in which it easily gives double salts, compounds with water of crystallisation, and forms rose-coloured solutions. In this form rhodium readily gives double salts of the two types RhM_3Cl_6 and RhM_2Cl_5

alkalies, which form bleaching salts). Among the platinum metals, ruthenium and osmium have the most acid character, and although they give RuCl_4 and OsCl_4 they are easily oxidised to RuO_4 and OsO_4 by the action of chlorine in the presence of water; the latter are volatile, and may be distilled with the water and hydrochloric acid, from a solution containing other platinum metals.^{9b} Thus with respect to

—for example, $\text{K}_3\text{RhCl}_6 \cdot 3\text{H}_2\text{O}$ and $\text{K}_2\text{RhCl}_5 \cdot \text{H}_2\text{O}$. Solutions of the salts (at least, the ammonium salt) of the first kind give salts of the second kind when they are boiled. If a strong solution of potash is added to a red solution of rhodium chloride and boiled, a black precipitate of the hydroxide $\text{Rh}(\text{OH})_3$ is formed; but if the solution of potash is added little by little, it gives a yellow precipitate containing more water. When dissolved in acids, this yellow hydrate of rhodium oxide gives a yellow solution, which only becomes rose-coloured after being boiled. It is obvious that a change takes place here, similar to the transmutations of the salts of chromic oxide. It is also a remarkable fact that the black hydroxide, like many other oxidised compounds of the platinoid metals, does not dissolve in the ordinary oxygen acids, whilst the yellow hydroxide is easily soluble and gives yellow solutions, which deposit imperfectly crystallised salts. Metallic rhodium is easily obtained by igniting its oxygen and other compounds in hydrogen, or by precipitation with zinc. It resembles platinum, and has a sp. gr. of 12.1. At the ordinary temperature it decomposes formic acid into hydrogen and carbonic anhydride (Dewille). With the alkali sulphites, the salts of rhodium and iridium of the type RX_3 give sparingly soluble precipitates of double salts of the composition $\text{R}(\text{SO}_3\text{Na})_3 \cdot \text{H}_2\text{O}$, by means of which these metals may be separated from solution, and also from each other, for a mixture of these salts, when treated with strong sulphuric acid, gives a soluble iridium sulphate and leaves a red insoluble double salt of rhodium and sodium. It may be remarked that the oxides Ir_2O_3 and Rh_2O_3 are comparatively stable and are easily formed, and that they also form different double salts and compounds like the cobaltic compounds (for instance, luteo-salts, $\text{RHX}_3 \cdot 6\text{NH}_3$, roseo-salts, $\text{RHX}_3 \cdot \text{H}_2\text{O} \cdot 5\text{NH}_3$, and purpureo-salts, $\text{IrX}_3 \cdot 5\text{NH}_3$, &c.). **Iridious oxide**, Ir_2O_3 , is obtained by fusing iridious chloride and its compounds with sodium carbonate and treating the mass with water. The oxide is then left as a black powder, which, when strongly heated, is decomposed into iridium and oxygen; it is easily reduced, and is insoluble in acids, which indicates the feeble basic character of this oxide, in many respects resembling such oxides as cobaltic oxide, ceric or lead dioxide, &c. It does not dissolve when fused with potassium hydrogen sulphate. Rhodium oxide, Rh_2O_3 , is a far more energetic base. It dissolves when fused with potassium hydrogen sulphate.

From what has been said respecting the separation of platinum and rhodium it will be understood how the compounds of **iridium**, which is the main associate of platinum, are obtained. In describing the treatment of osmiridium we shall again have an opportunity of learning the method of extraction of the compounds of this metal, which has found a technical application in the form of its oxide, Ir_2O_3 ; this is obtained from many of the compounds of iridium by ignition with water, is easily reduced by hydrogen, and is insoluble in acids. It is used in painting on china, for giving a black colour. Iridium itself is more difficultly fusible than platinum, and when fused does not decompose acids or even aqua regia; it is extremely hard, and is not malleable; its sp. gr. is 22.4. In the form of powder it dissolves in aqua regia, and is even partially oxidised when heated in air, sets fire to hydrogen, and, in a word, closely resembles platinum. Heated in an excess of chlorine it gives iridic chloride, IrCl_4 , but this loses chlorine at 50° ; it is, however, more stable in the form of double salts, which have a characteristic black colour—for instance, $\text{Ir}(\text{NH}_4)_2\text{Cl}_6$ —but they give iridious chloride, IrCl_3 , when treated with sulphuric acid.

^{9b} We have yet to become acquainted with the two remaining associates of platinum—ruthenium and osmium—whose most important property is that they are oxidised

the types of combination, all the platinum metals, under certain circumstances, give compounds of the type RX_4 —for instance, RO_2 , RCl_4 , &c.

even when heated in air, and that they are able to give **volatile** oxides of the form RuO_4 and OsO_4 ; these have a powerful odour (like iodine and nitrous anhydride). Both these higher oxides are solids, the former being yellow and the latter white; they volatilise with great ease at 100° . They are known as **ruthenic** and **osmic anhydrides**, although their aqueous solutions (they both slowly dissolve in water) do not show an acid reaction, and although they do not even expel carbonic anhydride from potassium carbonate, do not give crystalline salts with bases, and their alkaline solutions partially deposit them again when boiled (an excess of water decomposes the salts). The formulæ OsO_4 and RuO_4 correspond with the vapour densities of these oxides. Thus Deville found the vapour density of osmic anhydride to be 128 (by the formula 127.5) referred to hydrogen. Tennant and Vauquelin discovered this compound, and Berzelius, Wöhler, Fritzsche, Struve, Deville, Claus, Joly, and others helped in its investigation; nevertheless there are still many questions concerning it which remain unsolved. It should be observed that RO_4 is the highest known form for an oxygen compound, and RH_4 the highest known form for a compound of hydrogen; whilst the highest forms of acid hydrates are SiH_4O_4 , PH_3O_4 , SH_2O_4 , $ClHO_4$ —all with four atoms of oxygen, and therefore in this number there is apparently the limit for the simple forms of combination of hydrogen and oxygen. In combination with *several* atoms of an element, or several elements, there may be more than O_4 or H_4 , but a molecule never contains more than four atoms of either O or H to one atom of another element. Thus the simplest forms of combination of hydrogen and oxygen are exhausted by the list RH_4 , RH_3 , RH_2 , RH , RO , RO_2 , RO_3 , RO_4 . The extreme members are RH_4 and RO_4 , and are only met with for such elements as carbon, silicon, osmium, ruthenium, which also give RCl_4 with chlorine. In these extreme forms, RH_4 and RO_4 , the compounds are the least stable (compare SiH_4 , PH_3 , SH_2 , ClH , or RuO_4 , MoO_3 , ZrO_2 , SrO), and easily give up part, or even the whole, of their oxygen or hydrogen.

The primary source from which the compounds of ruthenium and osmium are obtained is either **osmiridium** (the osmium predominates, from $IrOs$ to $IrOs_4$, sp. gr. from 16 to 21), which occurs in platinum ores (it is distinguished from the grains of platinum by its crystalline structure, hardness, and insolubility in aqua regia), or else those insoluble residues which are obtained, as we saw above, after treating platinum with aqua regia. Osmium predominates in these materials, which sometimes contain from 30 to 40 per cent. of it, and rarely more than 4 to 5 per cent. of ruthenium. The process for their treatment is as follows: they are first fused with 6 parts of zinc, and the zinc is then extracted with dilute hydrochloric acid. The osmiridium thus treated is, according to Fritzsche and Struve's method, then added to a fused mixture of potassium hydroxide and chlorate in an iron crucible; the mass, as it begins to evolve oxygen, acts on the metal, and the reaction afterwards proceeds spontaneously. The dark product is treated with water, and gives a solution of osmium and ruthenium in the form of soluble salts, R_2OsO_4 and R_2RuO_4 , whilst the insoluble residue contains a mixture of oxides of iridium (and some osmium, rhodium, and ruthenium), and grains of metallic iridium still unacted on. According to Frémy's method, the lumps of osmiridium are straightway heated to whiteness in a porcelain tube in a stream of air or oxygen, when the very volatile osmic anhydride is obtained directly, and is collected in a well-cooled receiver, whilst the ruthenium gives a crystalline sublimate of the dioxide, RuO_2 , which is, however, very difficultly volatile (it volatilises together with osmic anhydride), and therefore remains in the cooler portions of the tube; this method does not give volatile ruthenic anhydride, and the iridium and other metals are not oxidised or give non-volatile products. This method is simple, and at once gives pure dry osmic anhydride in the receiver, and ruthenium dioxide in the sublimate. The air which passes through the tube should be previously passed through sulphuric acid, not only in order to dry it, but also to remove the organic and reducing dust. The vapour of osmic anhydride must be powerfully cooled, and ultimately passed over caustic potash. A

But this is the highest form only for platinum and palladium. Further, the remaining platinum metals, like iron, give acids of the type

third mode of treatment, which is most frequently employed, was proposed by Wöhler, and consists in slightly heating (in order that the sodium chloride should not melt) an intimate mixture of osmiridium and common salt in a stream of moist chlorine. The metals then form compounds with chlorine and sodium chloride, whilst the osmium forms the chloride, OsCl_4 , which reacts with the moisture, and gives osmic anhydride, which is condensed. The ruthenium in this, as in the other processes, does not directly give ruthenic anhydride, but is always extracted as the soluble ruthenium salt, K_2RuO_4 , obtained by fusion with potassium hydroxide and chlorate or nitrate. When the orange-coloured ruthenate, K_2RuO_4 , is mixed with acids, the liberated ruthenic acid immediately decomposes into the volatile ruthenic anhydride and the insoluble ruthenic oxide: $2\text{K}_2\text{RuO}_4 + 4\text{HNO}_3 = \text{RuO}_4 + \text{RuO}_3 \cdot 2\text{H}_2\text{O} + 4\text{KNO}_3$. When once one of the above compounds of ruthenium or osmium is procured, it is easy to obtain all the remaining compounds, and by reduction (by metals, hydrogen, formic acid, &c.) the metals themselves.

Osmic anhydride, OsO_4 , is very easily deoxidised by many methods. It blackens organic substances, owing to reduction, and is therefore used in investigating vegetable and animal, and especially nerve, preparations under the microscope. Although osmic anhydride may be distilled in hydrogen, yet complete reduction is accomplished when a mixture of hydrogen and osmic anhydride is slightly ignited (just before it inflames). If osmium be placed in the flame it is oxidised, and gives vapours of osmic anhydride, which become reduced, and the flame gives a brilliant light. Osmic anhydride deflagrates like nitre on red-hot charcoal; zinc, and even mercury and silver, reduce osmic anhydride from its aqueous solutions into the lower oxides or metal; such reducing agents as hydrogen sulphide, ferrous sulphate or sulphurous anhydride, alcohol, &c., act in the same manner with great ease.

The lower oxides of osmium, ruthenium, and of the other elements of the platinum series are not volatile, and it is noteworthy that the other elements behave differently. On comparing SO_2 , SO_3 ; As_2O_3 , As_2O_5 ; P_2O_3 , P_2O_5 ; CO , CO_2 , &c., we observe a converse phenomenon; the higher oxides are less volatile than the lower. In the case of osmium all the oxides, with the exception of the highest, are non-volatile, and it may therefore be thought that this higher form is more highly constituted than the lower. It is possible that osmic oxide, OsO_2 , stands in the same relation to the anhydride as C_2H_4 to CH_4 —i.e., the lower oxide is perhaps Os_2O_4 , or is still more polymerised, which would explain why the lower oxides, having a greater molecular weight, are less volatile than the higher oxides, just as we saw in the case of the nitrogen oxides, N_2O and NO .

Ruthenium and osmium, obtained by the ignition or reduction of their compounds in the form of powder, have a density considerably less than in the fused form, and differ in this condition in their capacity for reaction; they are much more difficultly fused than platinum and iridium, although ruthenium is more fusible than osmium. *Ruthenium* in powder has a specific gravity of 8.5, the fused metal of 12.2; *osmium* in powder has a specific gravity of 20.0, and when semi-fused—or, more strictly speaking, agglomerated—in the oxyhydrogen flame, of 21.4, and when fused 22.5. The powder of slightly heated osmium oxidises very easily in the air, and when ignited burns like tinder, forming directly the odoriferous and highly poisonous osmic anhydride (hence its name, from the Greek word *ὀσμή*, or *ὀσμός*, odour); ruthenium also oxidises when heated in air, but with more difficulty, forming the oxide, RuO_2 . The oxides of the types RO , R_2O_3 , and RO_2 (and their hydrates) obtained by reduction from the higher oxides, and also from the chlorides, are analogous to those given by the other platinum metals, in which respect osmium and ruthenium closely resemble them. We may also remark that ruthenium has been found in the platinum deposits of Borneo in the form of *laurite*, Ru_3S_3 , in grey octahedra of sp. gr. 7.0.

For osmium, Moralt and Wischin (1893) obtained free osmic acid, H_2OsO_4 , by

RO_3 or hydrates, $\text{H}_2\text{RO}_4 = \text{RO}_2(\text{HO})_2$ (the type of sulphuric acid); but these, like ferric and manganic acids, are chiefly known in the form of salts of the composition K_2RO_4 or $\text{K}_2\text{R}_2\text{O}_7$ (like the dichromate). These salts are obtained, like the manganates and ferrates, by fusing the oxides, or even the metals themselves, with nitric, or, better still, potassium peroxide. They are soluble in water, are easily deoxidised and do not yield the acid anhydrides under the action of acids, but break up, either (like the ferrate) forming oxygen and a basic oxide (iridium and rhodium react in this manner, as they do not give higher forms of oxidation), or passing into a lower and higher form of oxidation—that is, reacting like a manganate (or partly like a nitrite or phosphite). Osmium and ruthenium react according to the latter form, as they are capable of giving **higher forms of oxidation**, OsO_4 and RuO_4 , and therefore their reactions of decomposition may be essentially represented by the equation: $2\text{OsO}_3 = \text{OsO}_2 + \text{OsO}_4$.¹⁰

decomposing K_2OsO_4 with water, and precipitating with alcohol in a current of hydrogen (because in air volatile OsO_4 is formed); with H_2S osmic acid gives $\text{OsO}_3(\text{HS})_2$ at the ordinary temperature.

Debray and Joly showed that ruthenic anhydride, RuO_3 , fuses at 25° , boils at 100° , and evolves oxygen when dissolved in potash, forming the salt KRuO_4 (not isomorphous with potassium permanganate).

Joly (1891), who studied the ruthenium compounds in greater detail, showed that the easily formed KRuO_4 gives $\text{RuKO}_4\text{RuO}_3$ when ignited, but it resembles KMnO_4 in many respects. In general, Ru has much in common with Mn. Joly (1889) also showed that if KNO_3 is added to a solution of RuCl_3 containing HCl , the solution becomes hot, and a salt, $\text{RuCl}_3\text{NO}_2\text{KCl}$, is formed, which enters into double decomposition and is very stable. Moreover, if RuCl_3 be treated with an excess of nitric acid, it forms a salt, $\text{RuCl}_3\text{NO}_2\text{H}_2\text{O}$, on heating (to boiling) and adding HCl . The vapour density of RuO_4 (Debray and Joly) corresponds to that formula.

¹⁰ Although palladium gives the same types of combination (with chlorine) as platinum, its reduction to RX_2 is incomparably easier than that of platinum chloride, and in the case of iridium it is also very easy. Iridic chloride, IrCl_4 , acts as an oxidising agent, readily parts with a fourth of its chlorine to a number of substances, readily evolves chlorine when heated, and it is only at low temperatures that chlorine and aqua regia convert iridium into iridic chloride. In disengaging chlorine, iridium more often and easily gives the very stable iridous chloride, IrCl_3 (this substance is perhaps $\text{Ir}_2\text{Cl}_7 = \text{IrCl}_2\text{IrCl}_4$)—which is insoluble in water, but soluble in potassium chloride (because it forms the double salt K_3IrCl_6)—than the dichloride, IrCl_2 . This compound, corresponding with IrX_2 , is very stable, and corresponds with the **basic oxide**, Ir_2O_3 , resembling the oxides Fe_2O_3 , Co_2O_3 . To this form there correspond ammoniacal compounds similar to those given by cobaltic oxide. Although iridium also gives an acid in the form of the salt $\text{K}_2\text{Ir}_2\text{O}_7$, it does not, like iron (and chromium), form the corresponding chloride, IrCl_6 . In general, in this as in the other elements, it is impossible to predict the chlorine compounds from those of oxygen. In this respect rhodium is very much like iridium (as platinum is like palladium). For RhCl_3 decomposes with extreme ease, whilst rhodium chloride, RhCl_3 , is very stable, like many of the salts of the type RhX_3 . There is as close a resemblance between osmium and ruthenium. As a rule this acid character is more developed in osmium than in platinum and iridium. In general, the platinum metals subject themselves to the periodic law with perfect clearness, and their investigation is greatly facilitated by this means.

Platinum and its analogues, like iron and its analogues, are able to form complex and comparatively stable cyanogen and ammonia compounds, corresponding with the ferrocyanides and the ammoniacal compounds of cobalt, which we have already considered in the preceding chapter.

If platinous chloride, PtCl_2 (insoluble in water), is added by degrees to a solution of potassium cyanide, it is completely dissolved (like silver chloride), and, on evaporating, the solution deposits rhombic prisms of **potassium platinocyanide**, $\text{PtK}_2(\text{CN})_4 \cdot 3\text{H}_2\text{O}$. This salt, like all those corresponding with it, has a remarkable play of colours, due to the phenomena of dichroism, and even polychroism, natural to all the platinocyanides. Thus it is yellow and reflects a bright-blue light. It is easily soluble in water, effloresces in air, then turns red, and at 100° orange, when it loses all its water. The loss of water does not destroy its stability—that is, it still remains unchanged, and its stability is further shown by the fact that it is formed when potassium ferrocyanide, $\text{K}_4\text{Fe}(\text{CN})_6$, is heated with platinum black. This salt, first obtained by Gmelin, shows a neutral reaction with litmus; it is exceedingly stable under the action of air, like potassium ferrocyanide, which it resembles in many respects. Thus the platinum in it cannot be detected by reagents such as sulphuretted hydrogen,^{10a} the potassium may be replaced by other metals by the action of their salts, so that it corresponds with a whole series of compounds, $\text{R}_2\text{Pt}(\text{CN})_4$, and it is stable, although the potassium cyanide and platinous salts, of which it is composed, individually easily undergo change. When treated with oxidising agents it passes, like the ferrocyanide, into a higher form of combination of platinum. If salts of silver be added to its solution, it gives a heavy white precipitate of silver platinocyanide, $\text{PtAg}_2(\text{CN})_4$, which, when treated with sulphuretted hydrogen, forms insoluble Ag_2S , and soluble **hydroplatinocyanic acid**, $\text{H}_2\text{Pt}(\text{CN})_4$. If potassium platinocyanide be mixed with an equivalent quantity of sulphuric acid, the hydroplatinocyanic acid liberated may be extracted by a mixture of alcohol and ether, which does not dissolve the K_2SO_4 formed. The ethereal solution, when evaporated in a desiccator, deposits bright-red crystals of the composition $\text{PtH}_2(\text{CN})_4 \cdot 5\text{H}_2\text{O}$. This acid colours litmus paper, liberates carbonic anhydride from sodium carbonate, and saturates alkalies, so that it presents an analogy to hydroferrocyanic acid.¹¹

^{10a} It may also, therefore, be classed among the 'complex' compounds.

¹¹ This acid character is explained by the influence of the platinum on the hydrogen, and by the attachment of the cyanogen groups. Thus, cyanuric acid, $\text{H}_3(\text{CN})_3\text{O}_3$, is an energetic acid compared with cyanic acid, HCNO . And the formation of a compound with five molecules of water of crystallisation, $[\text{PtH}_2(\text{CN})_4 \cdot 5\text{H}_2\text{O}]$, confirms the opinion

Ammonia, like potassium cyanide, has the faculty of easily reacting with platinum dichloride, forming compounds which are similar to those

that platinum is able to form compounds of still higher types than that expressed in its saline compounds.

A whole series of **platinocyanides** of the common type $\text{PtR}_2(\text{CN})_4, n\text{H}_2\text{O}$ is obtained by means of double decomposition with the potassium or hydrogen or silver salts. For example, the salts of sodium and lithium contain, like the potassium salt, three molecules of water. The sodium salt is soluble in water and alcohol. The ammonium salt has the composition $\text{Pt}(\text{NH}_4)_2(\text{CN})_4, 2\text{H}_2\text{O}$ and gives crystals which reflect blue and rose-coloured light. This ammonium salt decomposes at 300° , with evolution of water and ammonium cyanide, leaving a greenish **platinum dicyanide**, $\text{Pt}(\text{CN})_2$, which is insoluble in water and acid, but dissolves in potassium cyanide, hydrocyanic acid, and other cyanides. The same platinous cyanide is obtained by the action of sulphuric acid on the potassium salts in the form of a reddish-brown amorphous precipitate. The most characteristic of the platinocyanides are those of the alkaline earths. The magnesium salt, $\text{PtMg}(\text{CN})_4, 7\text{H}_2\text{O}$, crystallises in regular prisms, the side faces of which are of a metallic-green colour and the terminal planes dark blue. It shows a carmine-red colour along the main axis, and dark red along the lateral axis; it easily loses water, $(2\text{H}_2\text{O})$, at 40° and then turns blue (it then contains $5\text{H}_2\text{O}$, which is frequently the case with the platinocyanides). Its aqueous solution is colourless, and an alcoholic solution deposits yellow crystals. The remainder of the water is given off at 230° . It is obtained by saturating platinocyanic acid with magnesia, or else by double decomposition between the barium salt and magnesium sulphate. The strontium salt, $\text{SrPt}(\text{CN})_4, 4\text{H}_2\text{O}$, crystallises in milk-white plates having a violet and green iridescence. When it effloresces in a desiccator, its surfaces have a violet and metallic-green iridescence. A colourless solution of the barium salt, $\text{PtBa}(\text{CN})_4, 4\text{H}_2\text{O}$, is obtained by saturating a solution of hydroplatinocyanic acid with baryta, or by boiling the insoluble copper platinocyanide in baryta water. It crystallises in monoclinic prisms of a yellow colour, with blue and green iridescence; it loses half its water at 100° , and the whole at 150° . The ethyl salt, $\text{PtC}_2\text{H}_5)_2(\text{CN})_4, 2\text{H}_2\text{O}$, is also very characteristic; its crystals are isomorphous with those of the potassium salt, and are obtained by passing hydrochloric acid into an alcoholic solution of hydroplatinocyanic acid. The facility with which they crystallise, the regularity of their forms, and their remarkable play of colours render the preparation of the platinocyanides one of the most attractive lessons of the laboratory. The barium salt is often employed in experiments with the Röntgen rays in investigating the radio-active substances, as it becomes very phosphorescent under the influence of these rays.

By the action of chlorine or dilute nitric acid the platinocyanides are converted into salts of the composition $\text{PtM}_2(\text{CN})_6$, which corresponds with $\text{Pt}(\text{CN})_3, 2\text{KCN}$ —that is, they express the type of a non-existent form of oxidation of platinum, PtX_3 (i.e., of the oxide Pt_2O_3), just as potassium ferricyanide, $(\text{FeCy}_3, 3\text{KCy})$, corresponds with ferric oxide, and the ferrocyanide with ferrous oxide. The potassium salt of this series, $\text{PtK}_2(\text{CN})_6, 3\text{H}_2\text{O}$, forms regular brown prisms with a metallic lustre, and is soluble in water but insoluble in alcohol. Alkalies re-convert this compound into the ordinary platinocyanide, $\text{K}_2\text{Pt}(\text{CN})_4$, taking up the excess of cyanogen. It is remarkable that the salts of the type PtM_2Cy_6 contain the same amount of water of crystallisation as those of the type PtM_2Cy_4 . Thus, the salts of potassium and lithium contain three, and the salt of magnesium seven, molecules of water, like the corresponding salts of the type of platinous oxide. Moreover, neither platinum nor any of its associates gives any cyanogen compound corresponding with the oxide, i.e., having the composition PtK_2Cy_6 , just as there are no compounds higher than those which correspond to $\text{RCy}_3, n\text{MCy}$ for cobalt or iron. This would appear to indicate the absence of any such double complex cyanides. The phenomenon is perhaps connected with the faculty of cyanogen of giving tricyanogen polymerides, such as cyanuric acid, solid cyanogen chloride, &c. Under the action of an excess of chlorine, a solution of $\text{PtK}_2(\text{CN})_4$ gives (besides PtK_2Cy_6) a product, $\text{PtK}_2\text{Cy}_4\text{Cl}_2$, which

given by cobalt and are comparatively stable. But as ammonia does not contain any hydrogen easily replaceable by metals, and as ammonia

evidently contains the form PtX_4 , but at first the action of the chlorine (or the electrolysis of, or addition of dilute peroxide of hydrogen to, a solution of PtK_2Cy_4 , acidulated with hydrochloric acid) produces an easily soluble intermediate salt which crystallises in thin copper-red needles (Wilm, 1889, and others). It apparently corresponds to a compound $5PtK_2Cy_4 + PtK_2Cy_4Cl_2 + 24H_2O$. Under the action of an excess of ammonia, both these chlorine products are converted either completely or in part (according to Wilm, ammonia does not act upon PtK_2Cy_4) into $PtCy_2, 2NH_3$, i.e., a platino-ammonia compound (see further on). It is also necessary to pay attention to the fact that ruthenium and osmium—which, as we know, give higher forms of oxidation than platinum—are also able to combine with a larger proportion of potassium cyanide (but not of cyanogen) than platinum. Ruthenium forms a crystalline **hydroruthenocyanic acid**, $RuH_4(CN)_6$, which is soluble in water and alcohol, and corresponds with the salts $M_4Ru(CN)_6$. There are exactly similar osmic compounds—for example, $K_4Os(CN)_6, 3H_2O$. The latter is obtained in the form of colourless, sparingly soluble regular tablets on evaporating the solution obtained from a fused mixture of potassium osmiochloride, K_2OsCl_6 , and potassium cyanide. These osmic and ruthenic compounds fully correspond with potassium ferrocyanide, $K_4Fe(CN)_6, 3H_2O$, not only in their composition, but also in their crystalline form and reactions, again demonstrating the close analogy between iron, ruthenium, and osmium, which we have shown by giving these three elements a similar position (in the eighth group in the periodic system). For rhodium and iridium only salts of the same type as the ferricyanides, M_3RCy_6 , are known, and for palladium only those of the type M_2PdCy_4 , which are analogons to the platinum salts. In all these examples a **constancy of the types** of the double cyanides is apparent. In the eighth group we have iron, cobalt, nickel, copper, and their analogues, ruthenium, rhodium, palladium, silver, and also osmium, iridium, platinum, gold. The double cyanides of iron, ruthenium, and osmium have the type $K_4R(CN)_6$; those of cobalt, rhodium, and iridium, the type $K_3R(CN)_6$; of nickel, palladium, and platinum, the types $K_2R(CN)_4$ and $K_2R(CN)_5$; and for copper, silver, and gold there are known $KR(CN)_2$, so that the presence of 4, 3, 2, and 1 atoms of potassium corresponds with the order of the elements in the periodic system. Those types which we have seen in the ferrocyanides and ferricyanides of iron repeat themselves in all the platinum metals, and this naturally leads to the conclusion that the formation of similar so-called double complex salts is of exactly the same nature as that of the ordinary salts. If, in expressing the union of the elements in the oxygen acids, the existence of an aqueous residue (hydroxyl group) be admitted, in which the hydrogen is replaced by a metal, we have then only to apply this mode of expression to the double salts, and the analogy will be obvious, if only we remember that Cl_2 , C_2N_2 , SO_3 , &c., are equivalent to O. So that wherever OH can stand there also can $Cl_2H_3(CN)_2H$, SO_4H , &c., stand. They all = X, and therefore, in point of fact, wherever X (= Cl or OH, &c.) can be placed, (Cl_2H) , (SO_4H) , &c., can also stand. And as $Cl_2H = Cl + HCl$ and $SO_4H = OH + SO_3$, &c., it follows that molecules HCl or SO_3 , or, in general, whole molecules—for instance, NH_3 , H_2O , salts, &c.—can annex themselves to a compound containing X. This is an indirect consequence of the law of substitution, which explains the origin of double salts, ammonia compounds, compounds with water of crystallisation, &c., by one general method. Thus, the double salt $MgSO_4, K_2SO_4$, according to this reasoning, *may be* considered as a substance of the same type as $MgCl_2$, namely, as $= Mg(SO_4K)_2$, and the alums as derived from $Al(OH)(SO_4)$, namely, as $Al(SO_4K)(SO_4)$. Without stopping to pursue this digression further, we shall apply these considerations to the type of the ferrocyanides and ferricyanides and their platinum analogues. Such a salt as K_2PtCy_4 may accordingly be regarded as $Pt(Cy_2K)_2$, like $Pt(OH)_2$; and such a salt as PtK_2Cy_2 as $PtCy(Cy_2K)_2$, the analogue of $PtX(OH)_2$, or $AlX(OH)_2$, and other compounds of the type RX_3 . Potassium ferricyanide and the analogous compounds of cobalt, iridium, and rhodium belong to the same type, with the same difference as there is between $RX(OH)_2$ and $R(OH)_3$, since $FeK_3Cy_6 = Fe(Cy_2K)_3$. Limiting myself to these considerations,

itself is able to combine with acids, the PtX_2 plays, as it were, the part of an acid with reference to the ammonia. Owing to the influence of

which may partially elucidate the nature of double salts, I shall now pass again to the complex saline compounds known for platinum.

(A) **Platinous chloride**, PtCl_2 , which is insoluble in water, forms **double salts with the metallic chlorides**. These double chlorides are soluble in water, and capable of crystallising. Hence, when a hydrochloric acid solution of platinous chloride is mixed with solutions of metallic salts and evaporated, it forms crystalline salts of a red or yellow colour. Thus, for example, the potassium salt, PtK_2Cl_4 , is red, and easily soluble in water; the sodium salt is soluble also in alcohol; the barium salt, $\text{PtBaCl}_4 \cdot 3\text{H}_2\text{O}$, is soluble in water, but the silver salt, PtAg_2Cl_4 , is insoluble and may be used for obtaining the remaining salts by means of double decomposition with their chlorides.

(B) On mixing solutions of potassium thiocyanate and potassium platinochloride, K_2PtCl_4 , they form a double thiocyanate, $\text{PtK}_2(\text{CNS})_4$, which is easily soluble in water and alcohol, crystallises in red prisms, and gives an orange-coloured solution, which precipitates salts of the heavy metals. The action of sulphuric acid on the lead salt of the same type gives the acid itself, $\text{PtH}_2(\text{SCN})_4$, which corresponds with these salts. The type of these compounds is evidently the same as that of the cyanides.

(C) A remarkable example of the complex compounds of platinum was observed by Schützenberger (1868). He showed that finely divided platinum in the presence of chlorine and carbonic oxide at 250° – 300° gives phosgene and a volatile compound containing platinum. The same substance is formed by the action of carbonic oxide on platinous chloride. It decomposes with an explosion in contact with water. Carbon tetrachloride dissolves a portion of this substance, and on evaporation gives crystals of $2\text{PtCl}_2 \cdot 3\text{CO}$, whilst the compound $\text{PtCl}_2 \cdot 2\text{CO}$ remains undissolved. When fused and sublimed it gives yellow needles of $\text{PtCl}_2 \cdot \text{CO}$, and in the presence of an excess of carbonic oxide $\text{PtCl}_2 \cdot 2\text{CO}$ is formed. These compounds are fusible (the first at 250° , the second at 142° , and the third at 195°). In this case (as in the double cyanides) combination takes place, because both carbonic oxide and platinous chloride are unsaturated compounds capable of further combination. The carbon tetrachloride solution absorbs NH_3 and gives $\text{PtCl}_2 \cdot \text{CO} \cdot 2\text{NH}_3$, and $\text{PtCl}_2 \cdot 2\text{CO} \cdot 2\text{NH}_3$, and these substances are analogous (Foerster, Zeisel, Jörgensen) to similar compounds containing complex amines (for instance, pyridine, $\text{C}_5\text{H}_5\text{N}$), instead of NH_3 , and ethylene, &c., instead of CO , so that here we have a whole series of complex platino-compounds. The compound $\text{PtCl}_2 \cdot \text{CO}$ dissolves in hydrochloric acid without change, and the solution disengages all the carbonic oxide when KCN is added to it, which shows that those forces which bind 2 molecules of KCN to PtCl_2 can also bind the molecule CO , or 2 molecules of CO . When the hydrochloric acid solution of $\text{PtCl}_2 \cdot \text{CO}$ is mixed with a solution of sodium acetate or acetic acid, it gives a precipitate of PtOCO , i.e., the Cl_2 is replaced by oxygen (probably because the acetate is decomposed by water). This oxide, PtOCO , splits up into $\text{Pt} + \text{CO}_2$ at 350° . PtSCO is obtained by the action of sulphuretted hydrogen upon $\text{PtCl}_2 \cdot \text{CO}$. All this leads to the conclusion that the group PtCO is able to assimilate $\text{X}_2 = \text{Cl}_2, \text{S}, \text{O}, \&c.$ (Mylius, Foerster, 1891). Pullinger (1891), by igniting spongy platinum at 250° , first in a stream of chlorine and then in a stream of carbonic oxide, obtained (besides volatile products) a non-volatile yellow substance which remained unchanged in air and disengaged chlorine and phosgene gas when ignited; its composition was $\text{PtCl}_6(\text{CO})_2$, which apparently proves it to be a compound of PtCl_2 and 2COCl_2 , as PtCl_2 is able to combine with oxychlorides, and forms somewhat stable compounds.

(D) The faculty of platinous chloride for forming stable compounds with divers substances shows itself in the formation of the compound $\text{PtCl}_2 \cdot \text{PCl}_3$ by the action of phosphorus pentachloride at 250° on platinum powder (Pd reacts in a similar manner, according to Fink, 1892). The product contains both phosphorus pentachloride and platinum, whilst the presence of PtCl_2 is shown in the fact that the action of water produces **chlorplatino-phosphorous acid**, $\text{PtCl}_2\text{P}(\text{OH})_3$.

the ammonia, the X_2 in the resultant compound will represent the same character as it has in ammoniacal salts; consequently the ammoniacal

(E) After the cyanides, the **double salts of platinum formed by sulphurous acid** are most distinguished for their stability and characteristic properties. This is all the more instructive, as sulphurous acid is only feebly energetic, and, moreover, in these, as in all its compounds, it exhibits a dual reaction. The salts of sulphurous acid, R_2SO_3 , either react as salts of a feeble dibasic acid, where the group SO_3 presents itself as bivalent, and consequently equal to X_2 , or else they react after the manner of salts of a monobasic acid containing the same residue, RSO_3 , as occurs in the salts of sulphuric acid. In sulphurous acid this residue is combined with hydrogen, $H(SO_3H)$, whilst in sulphuric acid it is united with the aqueous residue (hydroxyl), $OH(SO_3H)$. These two forms of action of the sulphites appear in their reactions with the platinum salts—that is to say, salts of both kinds are formed, and they both correspond with the type PtH_2X_4 . The one series of salts contain $PtH_2(SO_3)_2$, and their reactions are due to the bivalent residue of sulphurous acid, which replaces X_2 . The others, which have the composition $PtR_2(SO_3H)_4$, contain sulphoxyl. The latter salts will evidently react like acids; they are formed simultaneously with the salts of the first kind, and pass into them. These salts are obtained either by directly dissolving platinous oxide in water containing sulphurous acid, or by passing sulphurous anhydride into a solution of platinous chloride in hydrochloric acid. If a solution of platinous chloride or platinous oxide in sulphurous acid be saturated with sodium carbonate, it forms a white, sparingly soluble precipitate containing $PtNa_2(SO_3Na)_4 \cdot 7H_2O$. If this precipitate is dissolved in a small quantity of hydrochloric acid and left to evaporate at the ordinary temperature, it deposits a salt of the other type, $PtNa_2(SO_3)_2 \cdot H_2O$, in the form of a yellow powder, which is sparingly soluble in water. The potassium salt analogous to the first salt, $PtK_2(SO_3K)_4 \cdot 2H_2O$, is precipitated by passing sulphurous anhydride into a solution of potassium sulphite in which platinous oxide is suspended. A similar salt is known for ammonium, and with hydrochloric acid it gives a salt of the second kind, $Pt(NH_4)_2(SO_3)_2 \cdot H_2O$. If ammonio-chloride of platinum is added to an aqueous solution of sulphurous anhydride, it is first deoxidised and chlorine is evolved, forming a salt of the type PtX_2 ; a double decomposition then takes place with the ammonium sulphite, and a salt of the composition $Pt(NH_4)_2Cl_2(SO_3H)_4$ is formed (in a desiccator). The acid character of this substance is explained by the fact that it contains the elements SO_3H —sulphoxyl, with the hydrogen not yet displaced by a metal. On saturating a solution of this acid with potassium carbonate it gives orange-coloured crystals of a potassium salt of the composition $Pt(NH_4)_2Cl_2(SO_3K)_4$. Here it is evident that an equivalent of chlorine in $Pt(NH_4)_2Cl_2$ is replaced by the univalent residue of sulphurous acid. Among these salts, that of the composition $Pt(NH_4)_2Cl_2(SO_3H)_2 \cdot H_2O$ is very readily formed, and crystallises in well-formed colourless crystals; it is obtained by dissolving ammonium platinochloride, $Pt(NH_4)_2Cl_4$, in an aqueous solution of sulphurous acid. The difficulty with which sulphurous anhydride and platinum are separated from these salts indicates the same basic character in these compounds as is seen in the double cyanides of platinum. In their passage into a complex salt, the metal platinum and the group SO_2 modify their relations (compared with those of PtX_2 or SO_2X_2), just as the chlorine in the salts $KClO$, $KClO_3$, and $KClO_4$ is modified in its relations as compared with that in hydrochloric acid or potassium chloride.

(F) No less characteristic are the **double platinonitrites** (Co gives similar compounds). They correspond with nitrous acid, whose salts, RNO_2 , contain the univalent radicle, NO_2 , which is capable of replacing chlorine, so that the salts of this kind should form a common type, $PtR_2(NO_2)_4$, and such a salt of potassium has actually been obtained by mixing a solution of potassium platinochloride with a solution of potassium nitrite, when the liquid becomes colourless, especially if heated, indicating the change in the chemical distribution of the elements. As the liquid decolorises it gradually deposits sparingly soluble colourless prisms of the potassium salt, $K_2Pt(NO_2)_4$, which does not contain any water. With silver nitrate a solution of this salt gives a precipitate

compounds produced from PtX_2 will be salts in which X will be replaceable by various other haloids. **The platino-ammonium compounds** form compounds of PtX_2 with 2NH_3 , and with 4NH_3 . PtX_4 gives (not directly from PtX_4 and ammonia, but from the compounds of PtX_2 by the action of chlorine, &c.) similar compounds with 2NH_3 and with 4NH_3 .¹²

of silver platinonitrite, $\text{PtAg}_2(\text{NO}_2)_4$. The silver of this salt may be replaced by other metals by means of double decomposition with metallic chlorides. The sparingly soluble barium salt, when treated with an equivalent quantity of sulphuric acid, gives a soluble acid, which separates, under the receiver of an air-pump, in red crystals; this acid has the composition $\text{PtH}_2(\text{NO}_2)_4$. To the potassium salt, $\text{K}_2\text{Pt}(\text{NO}_2)_4$, there correspond (Vizes, 1892) $\text{K}_2\text{Pt}(\text{NO}_2)_4\text{Br}_2$ and $\text{K}_2\text{Pt}(\text{NO}_2)_4\text{Cl}_2$ and other compounds of the same type, K_2PtX_6 , where X is partly replaced by Cl or Br and partly by (NO_2) , showing a transition towards the type of the double salts like the platino-ammoniacal salts.

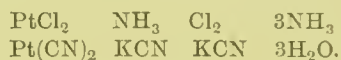
In all the preceding complex compounds of Pt we see a common type, $\text{PtX}_2 \cdot 2\text{MX}$ (i.e., of double salts corresponding to PtO) or $\text{PtM}_2\text{X}_4 = \text{Pt}(\text{MX}_2)_2$, corresponding to $\text{Pt}(\text{HO})_2$, with the replacement of O by its equivalent X_2 . The fact of so many of these complex compounds (see notes 12–14) being accumulated around Pt is doubtless no matter of chance. This is already seen in the many points of resemblance exhibited externally by these compounds, and is probably connected with the small energy of the salt-forming power of platinum and with its polyvalency in a state of combination. The elements prone to give such 'complex' compounds, like Cr, Co, Fe, Mo, W, &c., exhibit the same features, and there is reason for supposing that certain peculiarities in the reactions of organic compounds (for instance, the non-saline reactions of the products of metalepsis and the slow rate of many reactions, &c.) depend on the same causes as those which lead to the formation of 'complex' compounds. This subject, I think, presents one of the most important and interesting problems to be solved by the chemistry of the near future, and one which might also throw much light on the vaguely understood provinces of solutions and of the forces governing the formation of chemical compounds.

¹² Considering it unprofitable to discuss the merits of the numerous hypotheses which have been put forward at different times respecting the structure of the platino-ammonia compounds, as none of them brought any new facts to light, and all were limited to a pictorial representation of what was already known, I think it best, as far as possible, to unite the ammonia compounds of platinum with the other explained 'complex' compounds of platinum which have been more or less fully explained in the preceding notes (especially note 11). It seems to me that it is most important as a commencement to render clear the analogy in the formation of various complex compounds, and it is this analogy of the ammonia compounds with those containing water of crystallisation and double salts that forms the main object of the primary generalisation. We recognise in platinum, at all events, not only the four affinities expressed in the compound PtCl_4 , but a much larger number of them, if only the *summation of affinities* is actually possible. Thus, in sulphur we recognise not two, but a much greater number of affinities; it is clear that at least six affinities can act. So also among the analogues of platinum: osmic anhydride, OsO_4 , $\text{Ni}(\text{CO})_4$, PtH_2Cl_6 , &c., indicate the existence of at least eight affinities; whilst, in chlorine, judging from the compound $\text{KClO}_4 = \text{ClO}_3(\text{OK}) = \text{ClX}_7$, we must recognise at least seven affinities, instead of the one usually accepted. The latter mode of calculating affinities is a tribute to that period of the development of science when only the simplest hydrogen compounds were considered, and when all complex compounds were entirely neglected (they were placed in the class of molecular compounds). This is insufficient for the present state of knowledge, because we find that, in complex compounds, as in the most simple, the same constant types or modes of equilibrium are repeated, and the character of certain elements is greatly modified in the passage from the most simple into very complex compounds.

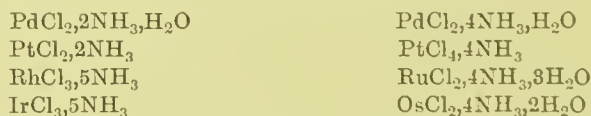
Judging from the most complex platino-ammonium compounds, $\text{PtCl}_4 \cdot 4\text{NH}_3$, we should admit the possibility of the formation of compounds of the type PtX_4Y_4 , where

If ammonia acts on a boiling solution of platinous chloride in hydrochloric acid, it produces the green salt of Magnus (1829), $\text{PtCl}_2 \cdot 2\text{NH}_3$, insoluble in water and hydrochloric acid. But, judging by its reactions, this salt has twice the above formula. Thus, Gros (1837), on boiling Magnus' salt with nitric acid, observed that half the chlorine was replaced by the residue of nitric acid and half the platinum was disengaged: $2\text{PtCl}_2(\text{NH}_3)_2 + 2\text{HNO}_3 = \text{PtCl}_2(\text{NO}_3)_2(\text{NH}_3)_4 + \text{Pt} + 2\text{HCl}$. The Gros' salt thus obtained, $\text{PtCl}_2(\text{NO}_3)_2 \cdot 4\text{NH}_3$ (if Magnus' salt

$\text{Y}_4 = 4\text{X}_2 = 4\text{NH}_3$, and this shows that those forces which form such a characteristic series of double platinocyanides, $\text{PtK}_2(\text{CN})_4 \cdot 3\text{H}_2\text{O}$, probably also determine the formation of the higher ammonia derivatives, as is seen on comparing—



Moreover, it is obviously much more natural to ascribe the faculty for combination with $n\text{Y}$ to the whole of the acting elements—that is, to PtX_2 or PtX_4 , and not to platinum alone. Naturally such compounds are not produced with every Y. With certain X's there only combine certain Y's. The best known and most frequently formed compounds of this kind are those with water—that is, compounds with water of crystallisation. Compounds with salts are double salts; also we know that similar compounds are frequently formed by means of ammonia. Salts of zinc, ZnX_2 , copper, CuX_2 , silver, AgX , and many others give similar compounds; but these and many other ammonio-metallic saline compounds are unstable, and readily part with their combined ammonia, and it is only in the elements of the platinum group and in the group of the analogues of iron that we observe the faculty to form stable ammonio-metallic compounds. It must be remembered that the metals of the platinum and iron groups are able to form several high grades of oxidation which have an acid character, and consequently in the lower degrees of combination there yet remain affinities capable of retaining other elements, and they probably retain ammonia, and hold it the more stably, because all the properties of the platinum compounds are rather acid than basic—that is, PtX_n recalls HX or SnX_n or CX_n rather than KX , CaX_2 , BaX_2 , &c., and ammonia naturally will rather combine with an acid than with a basic substance. Further, a dependence, or certain connection of the forms of oxidation with the ammonia compounds, is seen on comparing the following compounds:—



We know that platinum and palladium give compounds of lower types than iridium and rhodium, whilst ruthenium and osmium give the highest forms of oxidation; this shows itself in this case also. We have purposely cited the same compounds with 4NH_3 for osmium and ruthenium as we have for platinum and palladium, and it is then seen that Ru and Os are capable of retaining $2\text{H}_2\text{O}$ and $3\text{H}_2\text{O}$, besides Cl_2 and NH_3 , which the compounds of platinum and palladium are unable to do. The same ideas which were developed in note 35, Chap. XXII., respecting the cobaltia compounds are perfectly applicable to the present case, i.e., to the **platinia** compounds or ammonia compounds of the platinum metals, among which Rh and Ir give compounds which are completely analogous to the cobaltia compounds.

Iridium and rhodium, which readily give compounds of the type RX_3 , give compounds (Chaus) of the type $\text{IrX}_3 \cdot 5\text{NH}_3$, of a rose colour, and $\text{RhX}_3 \cdot 5\text{NH}_3$, of a yellow colour. Jørgensen, in his researches on these compounds, showed their entire analogy with the cobalt compounds, as was to be expected from the periodic system.

belongs to the type PtX_2 , then Gros' salt is of the type PtX_4 , is soluble in water, and the elements of nitric acid, but not the chlorine, contained in it are capable of submitting themselves readily to double saline decomposition. Thus, silver nitrate does not enter into double decomposition with the chlorine of Gros' salt.^{12a} Most instructive was the circumstance that Gros, by acting on his salt with hydrochloric acid, succeeded in substituting the residue of nitric acid in it by chlorine, and the chlorine thus introduced easily reacted with silver nitrate. Thus, it appeared that Gros' salt contained two varieties of chlorine—one which reacts readily and the other with difficulty. The composition of Gros' first salt is $\text{PtCl}_2(\text{NH}_3)_4(\text{NO}_3)_2$; it may be converted into $\text{PtCl}_2(\text{NH}_3)_4(\text{SO}_4)$, and in general into $\text{PtCl}_2(\text{NH}_3)_4\text{X}_2$.¹³

The salt of Magnus when boiled with a solution of ammonia gives the salt (of Reiset's first base) $\text{PtCl}_2(\text{NH}_3)_4$, and this, when treated with bromine, forms the salt $\text{PtCl}_2\text{Br}_2(\text{NH}_3)_4$, which has the same composition and reactions as Gros' salt. To Reiset's salts, $\text{PtCl}_2(\text{NH}_3)_4$, there corresponds a soluble, colourless, crystalline **hydroxide**, $\text{Pt}(\text{OH})_2(\text{NH}_3)_4$, having the properties of a powerful and very energetic **alkali**; it attracts carbonic anhydride from the atmosphere, precipitates metallic salts like potash, saturates active acids, even sulphuric, forming colourless (with nitric, carbonic, and hydrochloric acids) or yellow (with sulphuric acid) salts of the type $\text{PtX}_2(\text{NH}_3)_4$.¹⁴ The comparative stability of such

^{12a} Exactly the same was subsequently observed in certain chromic and cobaltic salts, and the matter must be understood to depend upon the situation of the chlorine with respect to the monatomic elements in the complex compounds.

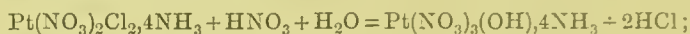
¹³ Subsequently a whole series of such compounds was obtained with various elements in the place of the (non-reacting) chlorine, and all these substituents, like the chlorine, reacted with difficulty, whilst the second portion of the X's introduced into such salts easily underwent reaction. This formed the most important reason for the interest which the study of the composition and structure of the platino-ammonium salts presented to many chemists, such as Reiset, Blomstrand, Peyrone, Raefski, Gerhardt, Buckton, Clève, Thomsen, Jørgensen, Kournakoff, Werner, and others. The salts, $\text{PtX}_4, 2\text{NH}_3$, discovered by Gerhardt, also exhibited several different properties in the two pairs of X's. In the remaining platino-ammonium salts all the X's appear to react alike.

The quality of the X's, retainable in the platino-ammonium salts, may be considerably modified, and they may frequently be wholly or partially replaced by hydroxyl. For example, the action of ammonia on the nitrate of Gerhardt's base, $\text{Pt}(\text{NO}_3)_4, 2\text{NH}_3$, in a boiling solution, gradually produces a yellow crystalline precipitate which is nothing else than a **basic hydrate** or **alkali**, $\text{Pt}(\text{OH})_4, 2\text{NH}_3$. It is sparingly soluble in water, but gives soluble salts, $\text{PtX}_4, 2\text{NH}_3$ directly with acids. The stability of this hydroxide is such that potash does not expel ammonia from it, even on boiling, and it does not change below 130° . Similar properties are shown by the hydroxide $\text{Pt}(\text{OH})_2, 2\text{NH}_3$ and the oxide $\text{PtO}, 2\text{NH}_3$ of Reiset's second base. But the hydroxides of the compounds containing 4NH_3 are particularly remarkable. The presence of ammonia renders them soluble and energetic. The brevity of this work does not permit us, however, to mention many interesting particulars in connection with this subject.

¹⁴ Hydroxides are known corresponding with Gros' salts, which contain one hydroxyl group in the place of that chlorine or haloid which in Gros' salts reacts with difficulty,

compounds, and the existence of many other compounds analogous to them, endow them with a particular chemical interest. Thus

and these hydroxides do not at once show the properties of alkalis, just as the chlorine which stands in the same place does not react distinctly; but still, after the prolonged action of acids, this hydroxyl group is also replaced by acids. Thus, for example, the action of nitric acid on $\text{Pt}(\text{NO}_3)_2\text{Cl}_2, 4\text{NH}_3$ causes the non-active chlorine to react, but in the product all the chlorine is not replaced by NO_3 , but only one half, the other half being replaced by the hydroxyl group:



and this is particularly characteristic, because here the hydroxyl group has not reacted with the acid—an evident sign of the non-alkaline character of this residue. Here it is observable that the reactions of these substances (and probably of many other 'complex' salts) present some resemblance to many of the reactions proper to organic substances where the element of time plays a great part.

To the common properties of the platino-ammonium salts we must add not only their **stability** (feeble acids and alkalis do not decompose them, the ammonia is not evolved by heating, &c.), but also the fact that the ordinary reactions of platinum are concealed in them to as great an extent as those of iron in the ferricyanides. Thus, neither alkalis nor hydrogen sulphide will separate the platinum from them. For example, sulphuretted hydrogen in acting on Gros' salts gives sulphur, removes half the chlorine by means of its hydrogen, and forms salts of Reiset's first base. This may be understood or explained by considering the platinum in the molecule as covered, walled up by the ammonia, or situated in the centre of the molecule, and therefore inaccessible to reagents. On this assumption, however, we should expect to find clearly expressed ammoniacal properties, and this is not the case. Thus, ammonia is easily decomposed by chlorine, whilst in acting on the platino-ammonium salts containing PtX_2 and 2NH_3 or 4NH_3 , chlorine combines and does not destroy the ammonia; it converts Reiset's salts into those of Gros and Gerhardt. Thus, from $\text{PtX}_2, 2\text{NH}_3$ there is formed $\text{PtX}_2\text{Cl}_2, 2\text{NH}_3$, and from $\text{PtX}_2, 4\text{NH}_3$ the salt of Gros' base $\text{PtX}_2\text{Cl}_2, 4\text{NH}_3$. This shows that the amount of chlorine which combines is not dependent on the amount of ammonia present, but is due to the basic properties of platinum. Owing to this some chemists suppose the ammonia to be inactive or passive in certain compounds. It appears to me that these relations, these modifications in the usual properties of ammonia and platinum are explained directly by their mutual combination. Sulphur, in sulphurous anhydride, SO_2 , and hydrogen sulphide, SH_2 , is naturally one and the same, but if we only knew of it in the form of hydrogen sulphide, then, having obtained it in the form of sulphurous anhydride, we should consider its properties as hidden. The oxygen in magnesia, MgO , and that in nitric peroxide, NO_2 , are so different that there is no resemblance. We are accustomed to judge the metals by their saline compounds with haloid groups, and ammonia by its compounds with acid substances, and here, in the platino-compounds, if we assume the platinum to be bound to the entire mass of the ammonia—to its hydrogen and nitrogen—we shall understand that both the platinum and ammonia modify their characters. Far more complicated is the question why a portion of the chlorine (and other haloid simple and complex groups) in Gros' salts acts in a different manner from the other portion, and why only half of it acts in the usual way. But this also is not an exclusive case. The chlorine in potassium chlorate or in carbon tetrachloride does not react with metals with the same ease as the chlorine in the salts corresponding with hydrochloric acid. In this case it is united to oxygen and carbon, whilst in the platino-ammonium compounds it is united partly to platinum and partly to the platino-ammonium group. Many chemists, moreover, suppose that a part of the chlorine is united directly to the platinum and the other part to the nitrogen of the ammonia, and thus explain the difference of the reactions; but chlorine united to platinum reacts as well with a silver salt as the chlorine of ammonium chloride, NH_4Cl , or nitrosyl chloride, NOCl , although there is no doubt but that, in this case, there is a union between the chlorine and nitrogen. Hence,

Kournakoff (1889) obtained a series of corresponding compounds containing thiocarbamide, CSN_2H_4 , in the place of ammonia, $\text{PtCl}_2, 4\text{CSN}_2\text{H}_4$, and others corresponding with Reiset's salts. Hydroxylamine

it is necessary to explain the absence of a facile reactive capacity in a portion of the chlorine by the conjoint influence of the platinum and the ammonia on it, whilst the other portion may be admitted as being under the influence of the platinum only, and therefore as reacting as in other salts. By admitting a certain kind of stable union in the platino-ammonium grouping, it is possible to imagine that the chlorine does not react with its customary facility, because access to a portion of the atoms of chlorine in this complex grouping is difficult, and the chlorine union is not the same as we usually meet with in the saline compounds of chlorine.

In characterising the platino-ammonium compounds, it is necessary to bear in mind that compounds which already contain PtX_4 do not combine directly with NH_3 , and that such compounds as $\text{PtX}_4, 4\text{NH}_3$ only proceed from PtX_2 , and therefore it is natural to conclude that those affinities and forces which cause PtX_2 to combine with X_2 also cause it to combine with 2NH_3 . And having the compound $\text{PtX}_2, 2\text{NH}_3$, and supposing that in subsequently combining with Cl_2 it reacts with those affinities which produce the compounds of platinic chloride, PtCl_4 , with water, potassium chloride, potassium cyanide, hydrochloric acid, and the like, we explain not only the fact of combination, but also many of the reactions occurring in the transition of one kind of platino-ammonium salts into another. Thus, by this means we explain the following facts: (1) that $\text{PtX}_2, 2\text{NH}_3$ combines with 2NH_3 , forming salts of Reiset's first base; (2) and that this compound, $\text{PtX}_2, 2\text{NH}_3, 2\text{NH}_3$, when heated, or even when boiled in solution, again passes into $\text{PtX}_2, 2\text{NH}_3$ (which resembles the easy disengagement of water of crystallisation, &c.); (3) that $\text{PtX}_2, 2\text{NH}_3$ is capable of absorbing, under the action of the same forces, a molecule of chlorine, $\text{PtX}_2, 2\text{NH}_3, \text{Cl}_2$, which it then retains with energy, because it is attracted, not only by the platinum, but also by the hydrogen of the ammonia; (4) that the chlorine held in the compound (of Gerhardt) formed will have a position unusual in salts, which will explain a certain (although very feebly marked) difficulty of reaction; (5) that this does not exhaust the faculty of platinum for further combination (we need only recall the compound $\text{PtCl}_4, 2\text{HCl}, 16\text{H}_2\text{O}$), and that therefore both $\text{PtX}_2, 2\text{NH}_3, \text{Cl}_2$ and $\text{PtX}_2, 2\text{NH}_3, 2\text{NH}_3$ are still capable of combination, whence the latter, with chlorine, gives $\text{PtX}_2, 2\text{NH}_3, 2\text{NH}_3, \text{Cl}_2$, after the type of PtX_4Y_4 (and perhaps higher); (6) that Gros' compounds thus formed are readily re-converted into the salts of Reiset's first base when acted on by reducing agents; (7) that in Gros' salts, $\text{PtX}_2, 2\text{NH}_3, (\text{NH}_3\text{X})_2$, the newly attached chlorine will react with difficulty with salts of silver, &c., because it is attached both to the platinum and to the ammonia, for both of which it has an attraction; (8) that the faculty for further combination is not even yet exhausted in the type of Gros' salts, and that we actually have a compound of Gros' chlorine salt with platinous chloride and with platinic chloride; the salt $\text{PtSO}_4, 2\text{NH}_3, 2\text{NH}_3, \text{SO}_4$ combines further also with H_2O ; (9) that such a faculty of combination with new molecules is naturally more developed in the lower forms of combination than in the higher. Hence the salts of Reiset's first base—for example, $\text{PtCl}_2, 2\text{NH}_3, 2\text{NH}_3$ —both combine with water and give precipitates (soluble in water but not in hydrochloric acid) of double salts with many salts of the heavy metals—for example, with lead chloride, cupric chloride, and also with platinic and platinous chlorides (Buckton's salts). The latter compounds will have the composition $\text{PtCl}_2, 2\text{NH}_3, 2\text{NH}_3, \text{PtCl}_2$ —that is, the same composition as the salts of Reiset's second base, with which, however, they cannot be identical. Such an interesting case does actually exist. The first salt, $\text{PtCl}_2, 4\text{NH}_3, \text{PtCl}_2$, is green, insoluble in water and in hydrochloric acid, and is known as **Magnus' salt**, and the second, $\text{PtCl}_2, 2\text{NH}_3$, is **Reiset's yellow** and sparingly soluble (in water). They are isomeric (polymeric), and at the same time they easily pass into each other. If ammonia is added to a hot hydrochloric acid solution of platinous chloride, it forms the salt $\text{PtCl}_2, 4\text{NH}_3$, but in the presence of an excess of platinous chloride it gives Magnus' salt. On boiling the latter in ammonia it gives a colourless soluble salt of Reiset's first base, $\text{PtCl}_2, 4\text{NH}_3$, and if this is boiled,

and other substances corresponding with ammonia, also give similar compounds. The common properties and composition of such compounds show their great analogy to the cobaltia compounds (especially for ruthenium and iridium), and correspond with the fact that both the platinum metals and cobalt occur in the same (eighth) group.

with water, ammonia is disengaged, and a salt of Reiset's second base, $\text{PtCl}_2 \cdot 2\text{NH}_3$, is obtained.

A class of platino-ammonium isomerides (obtained by Millon and Thomsen) is also known. Buckton's salts—for example, the copper salt—were obtained by them from the salts of Reiset's first base, $\text{PtCl}_2 \cdot 4\text{NH}_3$, by treatment with a solution of cupric chloride, &c., and therefore, according to our method of expression, Buckton's copper salt will be $\text{PtCl}_2 \cdot 4\text{NH}_3 \cdot \text{CuCl}_2$. This salt is soluble in water, but not in hydrochloric acid. In it the ammonia must be considered as united to the platinum. But if cupric chloride is dissolved in ammonia, and a solution of platinous chloride in ammonium chloride added to it, a violet precipitate is obtained of the same composition as Buckton's salt, which, however, is insoluble in water, but soluble in hydrochloric acid. In this a portion, if not all, of the ammonia must be regarded as united to the copper, and it must therefore be represented as $\text{CuCl}_2 \cdot 4\text{NH}_3 \cdot \text{PtCl}_2$. This form is identical in composition but different in properties (is isomeric) with the preceding salt (Buckton's). The salt of Magnus is intermediate between them, $\text{PtCl}_2 \cdot 4\text{NH}_3 \cdot \text{PtCl}_2$; it is insoluble in water and hydrochloric acid. These and certain other instances of isomeric compounds in the series of the platino-ammonium salts throw a light on the nature of the compounds in question, just as the study of the isomerides of the carbon compounds has served and still serves as the chief cause of the rapid progress of organic chemistry. In conclusion, we may add that (according to the law of substitution) we must necessarily expect all kinds of intermediate compounds between the platino- and analogous ammonia derivatives on the one hand, and the complex compounds of nitrous acid on the other. Perhaps the instance of the reaction of ammonia upon osmic anhydride, OsO_4 , observed by Fritzsche, Frémy, and others, and more fully studied by Joly (1891), belongs to this class. The latter showed that when ammonia acts upon an alkaline solution of OsO_4 , the reaction proceeds according to the equation: $\text{OsO}_4 + \text{KHO} + \text{NH}_3 = \text{OsNKO}_3 + 2\text{H}_2\text{O}$. It might be imagined that in this case the ammonia is oxidised, probably forming the residue of nitrous acid (NO), while the type OsO_4 is deoxidised into OsO_2 , and a salt, $\text{OsO}(\text{NO})(\text{KO})$, of the type OsX_4 is formed. This salt crystallises well in light yellow octahedra. It corresponds to **osmiamic acid**, $\text{OsO}(\text{ON})(\text{HO})$, the anhydride of which, $[\text{OsO}(\text{NO})]_2\text{O}$, has the composition $\text{Os}_2\text{N}_2\text{O}_5$, which equals $2\text{Os} + \text{N}_2\text{O}_5$ to the same extent as the above-mentioned compound, PtCO_2 , equals $\text{Pt} + \text{CO}_2$ (see note 11).

CHAPTER XXIV

COPPER, SILVER, AND GOLD

THAT degree of analogy and difference which exists between iron, cobalt, and nickel repeats itself in the corresponding triads ruthenium, rhodium, and palladium, and osmium, iridium, and platinum. These nine metals form group VIII. of the elements in the periodic system, being the intermediate group between the even elements of the large periods and the uneven ones, among which we know zinc, cadmium, and mercury in group II. Copper, silver, and gold complete ¹ this transition, because their properties place them in proximity to nickel, palladium, and platinum on the one hand, and to zinc, cadmium, and mercury on the other. Just as Zn, Cd, and Hg ; Fe, Ru, and Os ; Co, Rh, and Ir ; Ni, Pd, and Pt, resemble each other in many respects, so also do Cu, Ag, and Au. Thus, for example, in atomic weight ($\text{Cu}=63.6$), and in all its properties, copper stands between $\text{Ni}=59$ and $\text{Zn}=65.4$. But as the transition from group VIII. to group II., where zinc is situated, cannot be otherwise than through group I., so in copper there are certain properties of the elements of group I. Thus it gives a suboxide, Cu_2O , and salts CuX , like the elements of group I., although at the same time it forms an oxide, CuO , and salts, CuX_2 , like nickel and zinc. In the form of the oxide, CuO , and of the salts, CuX_2 , copper is analogous to zinc, judging from the insolubility of the carbonates, phosphates, and similar salts, and by the isomorphism and other characters.² In the cuprous salts there is undoubtedly a great

¹ The perfectly unique position held by copper, silver, and gold in the periodic system of the elements and the degree of affinity which is found between them are all the more remarkable, as nature and practice have long isolated these metals from all others by having employed them—for example, for coinage—and determined their relative importance and value in conformity with the order (silver between copper and gold) of their atomic weights, &c.

² Cupric sulphate contains 5 molecules of water, $\text{CuSO}_4, 5\text{H}_2\text{O}$, and the isomorphous mixtures with $\text{ZnSO}_4, 7\text{H}_2\text{O}$ contain either 5 or 7 equivalents, according to whether copper or zinc predominates (Vol. II., p. 5). If there is a large proportion of copper, and if the mixture contains $5\text{H}_2\text{O}$, the form of the isomorphous mixture (triclinic) will be isomorphous with cupric sulphate, $\text{CuSO}_4, 5\text{H}_2\text{O}$, but if a large amount of zinc (or magnesium, iron, nickel, or cobalt) is present the form (rhombic or monoclinic) will be nearly the same

resemblance to those of silver ; thus, for example, silver chloride, AgCl , is characterised by its insolubility and capacity of combining with ammonia, and in this respect cuprous chloride closely resembles it, for it is also insoluble in water, and combines with ammonia and dissolves in it, &c. Its composition is also RCl , the same as AgCl , NaCl , KCl , &c., and silver in many compounds resembles, and is even isomorphous with, sodium ; so that this again justifies their being brought together. Silver chloride, cuprous chloride, and sodium chloride crystallise in the regular system. Besides which, the specific heats of copper and silver require that they should have the atomic weights ascribed to them. To the oxides Cu_2O and Ag_2O there are corresponding sulphides, Ag_2S and Cu_2S . These both occur in nature in crystals of the rhombic system, and, what is most important, copper glance contains an isomorphous mixture of them both, and retains the form of copper glance with various proportions of copper and silver, and therefore has the composition R_2S , where $\text{R}=\text{Cu}, \text{Ag}$.

Notwithstanding the resemblance between the atomic compositions of the cuprous, CuX , and silver, AgX , compounds, and that of the compounds of the alkali metals, KX , NaX , there is a considerable degree of difference between these two series of elements. This difference is clearly seen in the fact that the alkali metals belong to those elements which combine with extreme facility with oxygen and decompose water, whilst silver and copper are oxidised with difficulty, form less energetic bases, and do not decompose water, even at moderately high temperatures. Moreover, they displace hydrogen from only very few acids. The difference between them is also seen in the dissimilarity of the properties of many of the corresponding compounds. Thus cuprous oxide, Cu_2O , and silver oxide, Ag_2O , are insoluble in water ; the cuprous and silver carbonates, chlorides, and sulphates are also sparingly soluble in water. The oxides of silver and copper are also easily reduced to metal. This difference in properties is in intimate relation with that difference in the density of the metals which exists in this case. The alkali metals belong to the lightest metals, and copper and silver to the heaviest, and therefore the distance between the molecules in these metals is very dissimilar—it is greater for the former than the latter (tables on p. 46, Vol. II.).

Copper is one of the few metals which have long been known in a metallic form. The Greeks and Romans imported copper chiefly from the island of Cyprus—whence its Latin name, *cuprum*. It was known

as that of zinc sulphate, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$. Supersaturated solutions of each of these salts crystallise in that form and with that amount of water which is contained in a crystal of one or other of the salts brought into contact with the solution (Chap. XIV., note 27).

to the ancients before iron, and was used, especially when alloyed with other metals, for arms and domestic utensils. That copper was known to the ancients will be understood from the facts that it occurs, although rarely, in a **native state**, and that it is easily extracted from its other natural compounds. Among the latter are the oxygen compounds of copper. When ignited with charcoal, they easily give up their oxygen to it, and yield metallic copper; hydrogen also easily takes up the oxygen from copper oxide when heated. Copper occurs in a native state, sometimes in association with other ores, in many parts of the Urals and in Sweden, and in considerable masses in America, especially in the neighbourhood of the great American lakes; and also in Chili, Japan, and China. The oxygen compounds of copper are also of somewhat common occurrence in certain localities. In this respect certain deposits of the Urals are especially famous. The geological period of the Urals (Permian) is characterised by a considerable distribution of copper ores. Copper is met with in the form of **cuprous oxide**, or **suboxide of copper**, Cu_2O , and is then known as **red copper ore**, because it forms red masses which are not infrequently crystallised in the regular system. It is found much more rarely in the state of *cupric oxide*, CuO , and is then called **black copper ore**. The most common of the oxygenised compounds of copper are the **basic carbonates** corresponding with the oxides. That these compounds are undoubtedly of aqueous origin is apparent, not only from the fact that specimens are frequently found of a gradual transition from the metallic, sulphuretted, and oxidised copper into its various carbonates, but also from the presence of water in their composition, and from the laminar, reniform structure which many of them present. In this respect **malachite** is particularly well known: it is used as a green paint and also for ornaments, owing to the diversity of the shades of colour presented by the different layers of deposited malachite. The composition of malachite corresponds with the basic carbonate containing one molecule of cupric carbonate to one of hydroxide: $\text{CuCO}_3, \text{CuH}_2\text{O}_2$. In this form the copper frequently occurs in admixture with various sedimentary rocks, forming large strata, which confirms the aqueous origin of these compounds. There are many such localities in the Perm and other governments bounding the Urals. **Blue carbonate of copper**, or **azurite**, is also often met with in the same localities: it contains the same ingredients as malachite, but in a different proportion, its composition being $\text{CuH}_2\text{O}_2, 2\text{CuCO}_3$. Both these substances may be obtained artificially by the action of the alkali carbonates on solutions of cupric salts at various temperatures. These native carbonates are often used for the extraction of copper, especially as they very readily give metallic copper, evolving water and carbonic

anhydride when ignited, and leaving the easily reducible cupric oxide. Copper is, however, also often met with in the form of the sulphides. The sulphides of copper generally occur in chemical combination with the sulphides of iron.³ These copper-sulphur compounds (copper pyrites, CuFeS_2 , variegated copper ore, Cu_3FeS_3 , &c.) generally occur in veins in a rock gangue.

The extraction of copper from its oxide ores does not present any difficulty, because the copper, when ignited with charcoal and melted, is reduced from the impurities which accompany it. This mode of smelting copper ores is carried on in cupola or cylindrical furnaces, fluxes forming a slag being added to the mixture of ore and charcoal. The smelted copper still contains sulphur, iron, and other metallic impurities, from which it is freed by fusion in reverberatory furnaces, with access of air to the surface of the molten metal, as the iron and sulphur are more easily oxidised than the copper. The iron then separates as oxides, which collect in the slag.⁴ Copper is frequently

³ Iron pyrites, FeS_2 , very often contains a small quantity of copper sulphide (see Chap. XXII., note 2a), and in burning the iron pyrites for sulphurous anhydride the copper oxide remains in the residue, from which the copper is often extracted with profit. For this purpose the whole of the sulphur is not burnt off from the iron pyrites, but a portion is left behind in the ore, which is then slowly ignited (roasted) with access of air. Cupric sulphate is then formed, and is extracted by water; or, as is better and more frequently done, the residue from the roasting of the pyrites is roasted with common salt, and the solution of cupric chloride obtained by lixiviating is precipitated with iron. A far greater amount of copper is obtained from other sulphuretted ores. Among these **copper glance**, Cu_2S , is more rarely met with. It has a metallic lustre, is grey, generally crystalline, and is obtained in admixture with organic matter; so that there is no doubt that its formation is due to the reducing action of the latter on solutions of cupric sulphate. **Variegated copper ore**, which crystallises in octahedra, not infrequently forms an admixture in copper glance: it has a metallic lustre, and is reddish-brown; it has a superficial play of colours, due to oxidation proceeding on its surface. Its composition is Cu_3FeS_3 . But the most common and widely distributed copper ore is **copper pyrites**, which crystallises in regular octahedra; it has a metallic lustre, a sp. gr. of 4.0, and a yellow colour. Its composition is CuFeS_2 . It must be remarked that the sulphurous ores of copper are oxidised in the presence of water containing oxygen in solution, and form cupric sulphate or blue vitriol, which is readily soluble in water. If this water contains calcium carbonate, gypsum and cupric carbonate are formed by double decomposition: $\text{CuSO}_4 + \text{CaCO}_3 = \text{CuCO}_3 + \text{CaSO}_4$. Hence copper sulphide in the form of different ores must be considered as the primary product, and the many other copper ores as secondary products, formed by water. This is confirmed by the fact that at the present time the water extracted from many copper mines contains cupric sulphate in solution. From this liquid it is easy to extract cupric oxide by the action of organic matter and various impurities of water. Hence metallic copper is sometimes found in natural products of the modification of copper sulphide, and is probably deposited by the action of organic matter present in the water. Copper salts have been found in the ash of certain plants.

⁴ Oxidised ores rich in copper are very rare; the sulphur ores are of more common occurrence, but the extraction of the copper from them is much more difficult. The problem here consists not only in the removal of the sulphur, but also in the removal of the iron combined with the sulphur and copper. This is attained by a whole series of

refined (especially from Fe) by electrolysis. The impure copper forming the anode is immersed in a solution of CuSO_4 , and the refined copper

operations, after which there sometimes still remains the extraction of the metallic silver which generally accompanies the copper, although in but small quantity. These processes commence with the roasting—i.e., calcination—of the ore with access of air, by which means the sulphur is converted into sulphurous anhydride. It should here be remarked that iron sulphide is more easily oxidised than copper sulphide, and therefore the greater part of the iron in the residue from roasting is no longer in the form of sulphide but of oxide of iron. The roasted ore is mixed with charcoal and silicious fluxes, and smelted in a cupola furnace. The iron then passes into the slag, because its oxide gives an easily fusible mass with the silica, whilst the copper, in the form of sulphide, fuses and collects under the slag. The greater part of the iron is removed from the mass by this smelting. The resultant *coarse metal* is again roasted in order to remove the greater part of the sulphur from the copper sulphide, and to convert the metal into oxide, after which the mass is again smelted. These processes are repeated several times, according to the richness of the ore. During these smeltings a portion of the copper is already obtained in a metallic form, because copper sulphide gives metallic copper with the oxide ($\text{CuS} + 2\text{CuO} = 3\text{Cu} + \text{SO}_2$). We shall not describe the furnaces used or the details of this process here, but the above remarks include the explanation of those chemical processes which are accomplished in the various technical operations made use of in the process (for details see works on metallurgy).

Besides the smelting of copper there also exist methods for its extraction from solutions in the **wet way**, as it is called. Recourse is generally had to these methods for poor copper ores. The copper is brought into solution, from which it is separated by means of metallic iron or by other methods (by the action of an electric current). The sulphides are roasted in such a manner that the greater part of the copper is oxidised into cupric sulphate, whilst at the same time the corresponding iron salts are as far as possible decomposed. This process is based on the fact that the copper sulphides absorb oxygen when they are calcined in the presence of air, forming cupric sulphate. The roasted ore is treated with water to which acid is sometimes added, and after lixiviation the resultant solution containing copper is treated either with metallic iron or with milk of lime, which precipitates cupric hydroxide from the solution. Copper oxide ores poor in metal may be treated with dilute acids in order to obtain the copper oxides in solution, from which the copper is then easily precipitated either by iron or, as hydroxide, by lime. According to Hunt and Douglas's method, the copper in the ore is converted by calcination into the cupric oxide, which is brought into solution by the action of a mixture of solutions of ferrous sulphate and sodium chloride; the oxide converts the ferrous chloride into ferric oxide, forming copper chlorides, according to the equation: $3\text{CuO} + 2\text{FeCl}_2 = \text{CuCl}_2 + 2\text{CuCl} + \text{Fe}_2\text{O}_3$. The cupric chloride is soluble in water, whilst the cuprous chloride is dissolved in the solution of sodium chloride, and therefore all the copper passes into solution, from which it is precipitated by iron.

The same American metallurgists give the following wet method for extracting the Ag and Au occurring in many copper ores, especially in sulphur ores: (1) The Cu_2S is first converted into oxide by roasting in a calciner; (2) the CuO is extracted by the dilute sulphuric acid obtained in the fourth process, the Cu then passes into solution, while the Ag, Au, and oxides of iron remain behind in the residue (from which the noble metals may be extracted); (3) a portion of the copper in solution is converted into CuCl_2 (and CaSO_4 precipitated) by means of the CaCl_2 obtained in the fifth process; (4) the mixture of solutions of CuSO_4 and CuCl_2 is converted into the insoluble CuCl (salt of the suboxide) by the action of the SO_2 obtained by roasting the ore (in the first operation); sulphuric acid is then formed in the solution, according to the equation: $\text{CuSO}_4 + \text{CuCl}_2 + \text{SO}_2 + 2\text{H}_2\text{O} = 2\text{H}_2\text{SO}_4 + 2\text{CuCl}$; (5) the precipitated CuCl is treated with lime and water, and gives CaCl_2 in solution and Cu_2O in the residue; and lastly (6) the Cu_2O is reduced to metallic Cu by carbon in a furnace. According to Crookes's method the impure copper regulus obtained by roasting and smelting the ore is broken up and immersed

is deposited on the cathode (certain other impurities, such as Ag, Sb, Sn, Bi, &c., fall as a sediment from the anode).

Copper is characterised by its red colour, which distinguishes it from all other metals. Pure copper, distinguished for its great electro-conductivity (it is employed for conducting electric currents), is soft, and may be beaten out by a hammer at the ordinary temperature, and when hot may be rolled into very thin sheets. Extremely thin leaves of copper transmit a green light. The tenacity of copper is also considerable, and next to iron it is one of the most useful metals in this respect. Copper wire of 1 sq. millimetre in section only breaks under a weight of 30–45 kilograms (according to its purity). The specific gravity of copper is 8.8, unless it contains cavities, due to the fact that molten copper absorbs oxygen from the air, which is disengaged on cooling, thus giving a porous mass whose density is much less. Rolled copper, and also that which is deposited by the electric current, have a comparatively high density. Copper melts at a bright-red heat, about 1050° , although below the temperature at which many kinds of cast iron melt. At a high temperature it is converted into vapour, which communicates a green colour to the flame. Both native copper and that cooled from a molten state crystallise in regular octahedra. Copper is not oxidised in dry air at the ordinary temperature; but when calcined it becomes coated with a layer of oxide, and it does not burn

repeatedly in molten lead, which extracts the Ag and Au occurring in the regulus. The regulus is then heated in a reverberatory furnace to run off the lead, and is then smelted for Cu.

Prof. Schtukenberg proposes to extract the copper often present as carbonate in siliceous and argillaceous deposits in the Urals by means of the crude acetic acid obtained in the dry distillation of wood. The carbonate is converted into soluble acetate of copper at the ordinary temperature, and the solution when heated deposits metallic copper, owing to the reducing action of the organic matter present in the crude acid. The cheapness and simplicity of this method render it particularly suitable for the Urals, where there are many such deposits (of a greenish colour), and where the dry distillation of wood is carried on on a large scale.

The copper brought into the market often contains small quantities of various impurities. Among these there are generally present iron, lead, silver, arsenic, and sometimes small quantities of oxides of copper. As copper, when mixed with a small amount of foreign substances, loses its tenacity to a certain degree, the manufacture of very thin sheet copper requires the use of Chili copper, which is distinguished for its great softness, and therefore when it is desired to have pure copper, it is best to take thin sheet copper, like that which is used in the manufacture of cartridges. But the purest copper is electrolytic copper—that is, that which is deposited from solution by the action of an electric current.

If the copper contains silver, as is often the case, it is used in gold refineries for the precipitation of silver from its solutions in sulphuric acid. Iron and zinc reduce copper salts, but copper reduces mercury and silver salts. The precipitate contains not only the silver which was previously in solution, but also all that which was in the copper. The silver solutions in sulphuric acid are obtained in the separation of silver from gold by treating their alloys with sulphuric acid, which only dissolves the silver.

even at the highest temperature. When calcined in air, copper forms either the red cuprous oxide or the black cupric oxide, according to the temperature and the quantity of air supplied. In air at the ordinary temperature, copper, as everyone knows, oxidises, turns brown, and becomes coated with a green coating of basic salts, due to the action of the damp air containing carbonic acid. If this action continue for a long time, the copper will become covered with a thick coating of basic carbonate, or the so-called verdigris (the *æruugo nobilis* of ancient statues). This is due to the fact that copper, although scarcely capable of oxidising by itself,⁵ in the presence of water and acids—even very feeble acids, like carbonic acid—absorbs oxygen from the air and forms salts, which is a very characteristic property of it (and also of lead).⁶

⁵ Schützenberger showed that when the basic carbonate of copper is decomposed by an electric current it gives, besides the ordinary copper, an allotropic form which grows on the negative platinum electrode (if its surface be smaller than that of the positive copper electrode), in the form of brittle crystalline growths of sp. gr. 8.1. It differs from ordinary copper by giving, not nitric oxide, but nitrous oxide, when treated with nitric acid, and in being very easily oxidised in air and coated with red shades of colour. It is possible that this is copper hydride, or copper which has occluded hydrogen. Spring (1892) observed that copper reduced from the oxide by hydrogen at the lowest possible temperature was pulverulent, while that reduced from CuCl_2 at a somewhat high temperature appeared in bright crystals. The same difference occurs with many other metals, and is probably partly due to the volatility of the metallic chlorides.

⁶ This is taken advantage of in practice; for instance, by pouring dilute acids over copper turnings on revolving tables in the preparation of copper salts, such as verdigris, or the basic acetate, $2\text{C}_4\text{H}_6\text{CuO}_4 \cdot \text{CuH}_2\text{O}_2 \cdot 5\text{H}_2\text{O}$, which is so much used as a green oil paint (i.e., with boiled linseed or drying oil). The capacity of copper for absorbing oxygen in the presence of acids is so great that it is possible by this means (by taking, for example, thin copper shavings moistened with sulphuric acid) to take up all the oxygen from a given volume of air, and this is even employed for the analysis of air.

The combination of copper with oxygen is aided not only by acids, but also by alkalies, although cupric oxide does not appear to have an acid character. Alkalies do not act on copper except in the presence of air, when they produce cupric oxide, which does not appear to combine with such alkalies as caustic potash or soda. But the action of ammonia is particularly distinct (Chap. V., note 2). In the action of a solution of ammonia not only is oxygen absorbed by the copper, but it also acts on the ammonia, and a definite quantity of ammonia is always acted on simultaneously with the passage of the copper into solution. The ammonia is then converted into nitrous acid, according to the reaction: $\text{NH}_3 + \text{O}_3 = \text{NHO}_2 + \text{H}_2\text{O}$, and the nitrous acid thus formed passes into the state of ammonium nitrite, NH_4NO_2 . In this manner three equivalents of oxygen are expended on the oxidation of the ammonia, and six equivalents of oxygen pass over to the copper, forming six equivalents of cupric oxide. The latter does not remain in the state of oxide, but combines with the ammonia.

A strong solution of common salt does not act on copper, but a dilute solution corrodes copper, converting it into the oxychloride—that is, in the presence of air. This action of salt water is evident in those cases where the bottoms of ships are coated with sheet copper. From what has been said above it will be evident that copper vessels should not be employed in the preparation of food, because this contains salts and acids which act on copper in the presence of air, and give copper salts, which are poisonous, and therefore the food prepared in untinned copper vessels may be poisonous. Hence tinned vessels are employed for this purpose—that is, copper vessels coated with a thin layer of tin, on which acid and saline solutions do not act.

Copper does not decompose water, and therefore does not disengage hydrogen from it either at the ordinary or at high temperatures. Nor does copper liberate hydrogen from the oxygen acids; ^{6a} these act on it in two ways: they either give up a portion of their oxygen, forming lower grades of oxidation, or else only react in the presence of air. Thus, when nitric acid acts on copper it evolves nitric oxide, the copper being oxidised at the expense of the nitric acid. In the same way copper converts sulphuric acid into the lower grade of oxidation—into sulphurous anhydride, SO_2 . In these cases the copper is oxidised to copper oxide, which combines with the excess of acid taken, and therefore forms a cupric salt, CuX_2 . Dilute nitric acid does not act on copper at the ordinary temperature; but when heated it reacts with great ease; dilute sulphuric acid does not act on copper except in presence of air.

Both the oxides of copper, Cu_2O and CuO , are unacted on by air, and, as already mentioned, they both occur in nature.^{6b} However, in the majority of cases copper is obtained in the form of cupric oxide and its salts, and the copper compounds used industrially generally belong to this type. This is due to the fact that the **cuprous compounds absorb oxygen** from the air and pass into cupric compounds. The cupric compounds may serve as the source for the preparation of cuprous oxide, because many reducing agents are capable of deoxidising the oxide into the suboxide. Organic substances are most generally employed for this purpose, and especially saccharine substances, which are able, in the presence of alkalis, to undergo oxidation at the expense of the oxygen of the cupric oxide, and to give acids which combine with the alkali: $2\text{CuO} - \text{O} = \text{Cu}_2\text{O}$. In this case the deoxidation of the copper may be carried further and metallic copper obtained, if only the reaction is aided by heat. Thus, for example, a fine powder of metallic copper may be obtained by heat-

^{6a} In contact with Pt, copper forms a galvanic couple, and is then acted on by HCl , with the evolution of hydrogen.

^{6b} Copper gives, besides the cuprous oxide, Cu_2O , and cupric oxide, CuO , two known higher forms of oxidation; but they have been little investigated, and even their composition is not well known. **Copper dioxide** (CuO_2 , or $\text{CuO}_2 \cdot \text{H}_2\text{O}$, perhaps $\text{CuO}_1\text{H}_2\text{O}_2$) is obtained by the action of hydrogen peroxide on cupric hydroxide, when the green colour of the latter is changed to yellow. It is very unstable, and is decomposed even by boiling water, with the evolution of oxygen, whilst the action of acids gives cupric salts, oxygen being also disengaged. A still higher **copper peroxide** is formed by heating a mixture of caustic potash, nitre, and metallic copper to a red heat, and by dissolving cupric hydroxide in solutions of the hypochlorites of the alkali metals. A slight heating of the soluble salt formed is enough for it to be decomposed into oxygen and copper dioxide, which is precipitated. Judging from Frémy's researches, the composition of the copper-potassic salt should be K_2CuO_4 . Perhaps this is a compound of the peroxides of potassium, K_2O_2 , and of copper, CuO_2 .

ing an ammoniacal solution of cupric oxide with caustic potash and grape sugar. But if the reducing action of the saccharine substance proceeds in the presence of a sufficient quantity of alkali in solution, and at not too high a temperature, cuprous oxide is obtained. To see this reaction clearly, it is not sufficient to take any cupric salt, because the alkali necessary for the reaction might precipitate cupric oxide—it is necessary to add previously some substance which will prevent this precipitation. Among such substances, tartaric acid, $C_4H_6O_6$, is one of the best. In the presence of a sufficient quantity of tartaric acid any amount of alkali may be added to a solution of cupric salt without producing a precipitate, because a soluble double salt of cupric oxide and alkali is then formed. If glucose (for instance, honey or molasses) is added to such an alkaline tartaric solution, and the temperature is slightly raised, it first gives a yellow precipitate (this is cuprous hydroxide, $CuHO$), and then, on boiling, a red precipitate of anhydrous) cuprous oxide. If such a mixture be left for a long time at the ordinary temperature, it deposits well-formed crystals of anhydrous cuprous oxide belonging to the regular system.⁷

⁷ Colourless solutions of cuprous salts may be obtained by the action of sulphurous or phosphorous acid and similar lower grades of oxidation on the blue solutions of the cupric salts. This is very clearly and easily effected by means of sodium thiosulphate, $Na_2S_2O_3$, which is oxidised in the process. Cuprous oxide can be obtained not only by the deoxidation of cupric oxide, but also directly from metallic copper itself, because the latter, in oxidising at a red heat in air, *first* gives **cuprous oxide**. It is prepared in this manner on a large scale by heating sheet copper rolled into spirals in reverberatory furnaces. Care must be taken that the air is not in great excess, and that the coating of red cuprous oxide formed does not begin to pass into the black cupric oxide. If the oxidised spiral sheet is then unbent, the brittle cuprous oxide falls away from the soft metal. The suboxide obtained in this manner fuses with ease. The cupric oxide, when calcined with finely divided copper (this copper powder may be obtained by many methods—for instance, by immersing zinc in a solution of a copper salt, or by igniting cupric oxide in hydrogen), gives the fusible cuprous oxide: $Cu + CuO = Cu_2O$. Both the native and the artificial cuprous oxides have a sp. gr. of 5.6. It is insoluble in water, and is not acted on by (dry) air. When heated with acids the suboxide forms a solution of a cupric salt and metallic copper; for example, $Cu_2O + H_2SO_4 = Cu + CuSO_4 + H_2O$. However, strong hydrochloric acid does not deposit metallic copper on dissolving cuprous oxide, which is due to the fact that the cuprous chloride formed is soluble in strong hydrochloric acid. Cuprous oxide also dissolves in a solution of ammonia, and in the absence of air gives a colourless solution, which turns blue in the air, absorbing oxygen, owing to the conversion of the cuprous oxide into cupric oxide. The blue solution thus formed may be again reconverted into a colourless solution by immersing a copper strip in it, because the metallic copper then **deoxidises the cupric oxide** in the solution **into cuprous oxide**. Cuprous oxide gives red glasses when fused with glass or with salts, forming vitreous alloys. Glass tinted with cuprous oxide is used for ornaments. This may be taken advantage of in testing for copper under the blowpipe by heating the copper compound with borax in the flame of a blowpipe; a red glass is obtained in the reducing flame, and a blue glass in the oxidising flame, owing to the conversion of the cuprous into cupric oxide.

Étard (1882), by passing sulphurous anhydride into a solution of cupric acetate

Cupric chloride, CuCl_2 , when ignited, gives cuprous chloride, CuCl , i.e., the salt corresponding with suboxide of copper, and therefore cuprous chloride is always formed when copper enters into reaction with chlorine at a high temperature. When copper is calcined with mercuric chloride, it forms cuprous chloride and vapours of mercury. The same substance is obtained on heating metallic copper in hydrochloric acid, hydrogen being disengaged; but this reaction only proceeds with finely divided copper, as hydrochloric acid acts very feebly on compact masses of copper, and, in the presence of air, gives cupric chloride. The green solution of cupric chloride is decolorised by metallic copper, cuprous chloride being formed; but this reaction is only accomplished with ease when the solution is very concentrated and when an excess of hydrochloric acid is present to dissolve the cuprous chloride formed. The addition of water to the solution precipitates the cuprous chloride, because it is less soluble in dilute than in strong hydrochloric acid. Many reducing agents which are able to take up half the oxygen from cupric oxide are able, in the presence of hydrochloric acid, to form cuprous chloride. Stannous salts, sulphurous anhydride, alkali sulphites, phosphorous and hypophosphorous acids, and many similar reducing agents act in this manner. The usual method of preparing cuprous chloride consists in passing sulphurous anhydride into a very strong solution of cupric chloride: $2\text{CuCl}_2 + \text{SO}_2 + 2\text{H}_2\text{O} = 2\text{CuCl} + 2\text{HCl} + \text{H}_2\text{SO}_4$. Cuprous chloride forms colourless cubic crystals which are insoluble in water. It is easily fusible, and even volatile. Fused with soda, CuCl forms crystals of Cu_2O . Under the action of oxidising agents, it passes into the cupric salt, and it absorbs oxygen from moist air, forming cupric oxychloride, $\text{Cu}_2\text{Cl}_2\text{O}$. **Aqueous ammonia** easily dissolves cuprous chloride as well as cuprous oxide; this solution also turns blue on exposure to the air. Thus, an ammoniacal solution of cuprous chloride serves as an excellent absorbent for oxygen; but this solution absorbs not only oxygen, but also certain other gases, for example, carbonic oxide and acetylene.*

obtained a white precipitate of cuprous sulphite, $\text{Cu}_2\text{SO}_3 \cdot \text{H}_2\text{O}$, whilst he obtained the same salt, of a red colour, from the double salt of sodium and copper; but no convincing proofs of isomerism are known in this case.

* The solubility of cuprous chloride in ammonia is due to the formation of compounds of the ammonia with the chloride. In a warm solution the compound $\text{NH}_3 \cdot 2\text{CuCl}$ is formed, and at the ordinary temperature $\text{CuCl} \cdot \text{NH}_3$. This salt is soluble in hydrochloric acid, and then forms a corresponding double salt of cuprous chloride and ammonium chloride. By the action of a certain excess of ammonia on a hydrochloric acid solution of cuprous chloride, very well-formed crystals, having the composition $\text{CuCl} \cdot \text{NH}_3 \cdot \text{H}_2\text{O}$, are obtained. Cuprous chloride is not only soluble in ammonia and hydrochloric acid, but it also dissolves in solutions of certain other salts, for example, sodium chloride, potassium chloride, sodium thiosulphate. All the solutions act as

When copper is oxidised with a considerable quantity of oxygen at a high temperature, or at the ordinary temperature in the presence of acids, and also when it decomposes acids, converting them into lower grades of oxidation (for example, when submitted to the action of nitric and sulphuric acids), it forms **cupric oxide**, CuO , or, in the presence of acids, cupric salts. Copper rust, or that black mass which forms on the surface of copper when it is calcined, consists of cupric oxide. The coating of oxidised copper is very easily separated from the metallic copper, because it is brittle and readily peels off when it is struck or immersed in water. Many copper salts (for instance, the nitrate and carbonate) leave oxide of copper ^{8a} in the form of friable black powder, after being ignited. If the ignition is carried further, Cu_2O may be formed from the CuO .^{8b} Anhydrous cupric oxide

very powerful deoxidising substances; for example, it is easy, by means of these solutions, to precipitate gold from its solutions: $\text{AuCl}_3 + 3\text{CuCl} = \text{Au} + 3\text{CuCl}_2$.

Among the other compounds corresponding with cuprous oxide, **cuprous iodide**, CuI , is worthy of remark. It is a colourless substance which is insoluble in water and sparingly soluble in ammonia (like silver iodide), but capable of absorbing it, in which respect it resembles cuprous chloride. It is remarkable from the fact that it is exceedingly easily formed from the corresponding cupric compound, CuI_2 . A solution of cupric iodide easily decomposes into iodine and cuprous iodide, even at the ordinary temperature, whilst cupric chloride only suffers a similar change on ignition. If a solution of a cupric salt is mixed with a solution of potassium iodide, the cupric iodide formed immediately decomposes into free iodine and cuprous iodide, which separates out as a precipitate. In this case the cupric salt acts in an oxidising manner.

Cuprous oxide, when treated with hydrofluoric acid, gives an insoluble cuprous fluoride, CuF . Cuprous cyanide is also insoluble in water, and is obtained by the addition of hydrocyanic acid to a solution of cupric chloride saturated with sulphurous anhydride. This cuprous cyanide, like silver cyanide, gives a double soluble salt with potassium cyanide. The double cyanide of copper and potassium is tolerably stable in the air, and enters into double decompositions with various other salts, like those double cyanides of iron with which we are already acquainted.

Copper hydride, CuH , also belongs to the number of the cuprous compounds. It was obtained by Würtz by mixing a hot (70°) solution of cupric sulphate with a solution of hypophosphorous acid, H_3PO_2 . The addition of the reducing hypophosphorous acid must be stopped when a brown precipitate makes its appearance, and when gas begins to be evolved. When gently heated it disengages hydrogen: it gives cuprous oxide when exposed to the air, burns in a stream of chlorine, and liberates hydrogen with hydrochloric acid: $\text{CuH} + \text{HCl} = \text{CuCl} + \text{H}_2$. Zinc, silver, mercury, lead, and many other heavy metals do not form such a compound with hydrogen, either under these circumstances or under the action of hydrogen at the moment of the decomposition of salts by a galvanic current. The greatest resemblance is seen between cuprous hydride and the hydrogen compounds of K, Na, Pd, Ca, and Ba.

^{8a} The oxide of copper obtained by igniting the nitrate is frequently used for organic analyses. It is hygroscopic and retains nitrogen (1.5 c.c. per gram) when the nitrate is heated *in vacuo* (Richards and Rogers, 1893).

^{8b} Oxide of copper is also capable of dissociating when heated. Debray and Joannis showed that it then disengages oxygen, whose maximum pressure is constant for a given temperature, providing that fusion does not take place (the CuO then dissolves in the molten Cu_2O); and that this loss of oxygen is followed by the formation of suboxide.

is very easily dissolved in acids, forming cupric salts, CuX_2 . They are analogous to the salts MgX_2 , ZnX_2 , NiX_2 , FeX_2 , in many respects. On adding potassium or ammonium hydroxide to a solution of a cupric salt, it forms a gelatinous blue precipitate of the hydrated oxide of copper, CuH_2O_2 , insoluble in water. The resultant precipitate is redissolved by an excess of ammonia, and gives a very beautiful azure-blue solution, of so intense a colour that the presence of small traces of cupric salts may be discovered by this means.⁹ An excess of potassium or sodium hydroxide does not dissolve cupric hydroxide. A hot solution gives a black precipitate of the anhydrous oxide instead of the blue precipitate, and the precipitate of the hydroxide of copper becomes granular and turns black when the solution is heated. This is due to the fact that the blue hydroxide is exceedingly unstable, and when slightly heated it loses the elements of water and gives the black anhydrous cupric oxide: $\text{CuH}_2\text{O}_2 = \text{CuO} + \text{H}_2\text{O}$.

Cupric oxide fuses at a strong heat, and on cooling forms a heavy crystalline mass, which is black, opaque, and somewhat tenacious. It is a feebly energetic base, so that not only do the oxides of the metals of the alkalis and alkaline earths displace it from its compounds, but

⁹ Cupric oxide and many of its salts are able to give definite, although unstable, **compounds with ammonia**. This faculty already shows itself in the fact that cupric oxide and its salts dissolve in aqueous ammonia, and also in the fact that salts of copper absorb ammonia gas. If ammonia is added to a solution of any cupric salt, it first forms a precipitate of cupric hydroxide, which then dissolves in an excess of ammonia. The solution thus formed, when evaporated or on the addition of alcohol, frequently deposits crystals of salts containing the elements both of the salt of copper taken and of ammonia. Several such compounds are generally formed. Thus cupric chlorido, CuCl_2 , according to Deherain, forms four compounds with ammonia—namely, with one, two, four, and six molecules of ammonia. The compounds of CuSO_4 with 1-5 NH_3 are mentioned in Chap. XXII., note 85.

The solution obtained by the action of aqueous ammonia and air on copper turnings (note 6) is remarkable for its faculty of **dissolving cellulose**, which is insoluble in water, dilute acids, and alkalis. Paper soaked in such a solution acquires the property of not rotting, of being difficultly combustible and waterproof, &c. It has therefore been applied, especially in England, to many practical purposes; for example, to the construction of temporary buildings, for covering roofs, &c. The composition of the substance held in solution is $\text{Cu}(\text{HO})_2, 4\text{NH}_3$.

If dry ammonia gas is passed over cupric oxide heated to 265° , a portion of the oxide of copper gives **copper nitride**, the oxygen of the copper oxide combining with the hydrogen and forming water. The oxide of copper which remains unchanged is easily removed by washing the resultant product with aqueous ammonia. Copper nitride is very stable, and is insoluble; it has the composition Cu_3N (i.e., the copper is here monatomic, as in Cu_2O), and is an amorphous green powder, which is decomposed when strongly ignited, and gives cuprous chlorido and ammonium chloride when treated with hydrochloric acid. Like the other nitrides, copper nitride, Cu_3N , has scarcely been investigated. Grainger (1892), by heating copper in the vapour of phosphorus, obtained hexagonal prisms of Cu_3P , which passed into Cu_6P (previously obtained by Abel) when heated in nitrogen. Arsenic is easily absorbed by copper, and its presence (like P), even in small quantities, has a great influence upon the properties of copper.

even such oxides as those of lead and silver precipitate it from solutions, which is partially due to these oxides being soluble, although but slightly so, in water. However, cupric oxide, and especially the hydroxide, easily combines with even the least energetic acids, and does not give any compounds with bases; but, on the other hand, it easily forms basic salts,^{9a} and in this respect outstrips magnesium and recalls the

^{9a} As a comparatively feeble base, oxide of copper easily forms both basic and double salts. As an instance we may mention the double salts composed of the dichloride, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, and potassium chloride. The double salt $\text{CuK}_2\text{Cl}_4 \cdot 2\text{H}_2\text{O}$ crystallises from solutions in *blue* plates, but when heated with substances taking up water easily gives *brown* needles, CuKCl_3 , and at the same time KCl , and this reaction is reversible at 92° , as was shown by Meyerhoffer (1889). With an excess of the copper salt, KCl gives another double salt, $\text{Cu}_2\text{KCl}_5 \cdot 4\text{H}_2\text{O}$, the transition temperature of which is 55° . The instances of equilibria which are encountered in such complex relations are embraced by the **law of phases** given by Gibbs (*Transactions of the Connecticut Academy of Sciences*, 1875-1878, in J. Willard Gibbs's memoir, *On the Equilibrium of Heterogeneous Substances*, and in a more accessible form in the works of H. W. Bakhuis Roozeboom and W. Meyerhoffer, to which sources we refer those desiring information respecting the law of phases). Gibbs calls '**bodies**,' substances (simple or compound) capable of forming homogeneous complexes (for instance, solutions or inter-combinations) of a varied composition; a **phase**—a mechanically separable portion of such bodies or of their homogeneous complexes (for instance, a vapour, liquid, or precipitated solid); **perfect equilibrium**—such a state of bodies and of their complexes as is characterised by a constant pressure at a constant temperature even under a change in the amount of one of the component parts (for instance, of a salt in a saturated solution), while an **imperfect equilibrium** is one for which such a change corresponds with a change of pressure (for instance, an unsaturated solution). The law of phases consists in the fact that: *n bodies give only a perfect equilibrium when $n+1$ phases participate in that equilibrium*; for example, in the equilibrium of a salt in its saturated solution in water there are two bodies (the salt and water) and three phases, namely, the salt, solution, and vapour, which can be mechanically separated from each other, and to this equilibrium there corresponds a definite pressure. At the same time, *n bodies may occur in $n+2$ phases, but only at one definite temperature and one pressure*; a change of one of these may bring about another state (perfect or not—equilibrium stable or unstable). Thus water when liquid at the ordinary temperature offers two phases (liquid and vapour), and is in perfect equilibrium (as also is ice below 0°); but water, ice, and vapour (three phases and only one body) can only be in equilibrium at 0° , and at the ordinary pressure; with a change of *t* there will remain either only ice and vapour or only liquid water and vapour; whilst with a rise of pressure not only will the vapour pass into the liquid (there again only remain two phases), but also the temperature of the formation of ice will fall (by about 7° per 1,000 atmospheres). The law of phases is applicable to the consideration of the formation of simple or double salts from saturated solutions and to a number of other purely chemical relations. Thus, for example, in the above-mentioned instance, when the bodies are KCl , CuCl_2 , and H_2O , perfect equilibrium (which here has reference to the solubility) consisting of four phases, corresponds to the following seven cases, considering only the phases (above 0°): $A = \text{CuCl}_2 \cdot 2\text{KCl} \cdot 2\text{H}_2\text{O}$; $B = \text{CuCl}_2 \cdot \text{KCl}$; $C = \text{CuCl}_2 \cdot 2\text{H}_2\text{O} \cdot \text{KCl}$, solution and vapour: (1) $A + B + \text{solution} + \text{vapour}$; (2) $A + C + \text{solution} + \text{vapour}$; (3) $A + \text{KCl} + \text{solution} + \text{vapour}$; (4) $A + B + C + \text{vapour}$ (it follows that $B + \text{KCl} + \text{solution}$ gives A); (5) $A + C + \text{KCl} + \text{vapour}$; (6) $B + C + \text{solution} + \text{vapour}$; and (7) $B + \text{KCl} + \text{solution} + \text{vapour}$. Thus above 92° , A gives $B + \text{KCl}$. The law of phases by bringing complex instances of chemical reaction under simple physical schemes and graphic methods of representation facilitates their study in detail and gives the means of seeking the

oxides of lead or mercury. Hence the hydroxide of copper dissolves in solutions of neutral cupric salts. The cupric salts are generally blue or green, because cupric hydroxide itself is coloured. But some of the salts in the anhydrous state are colourless.¹⁰

The commonest normal salt is **blue vitriol**, i.e., the normal cupric sulphate. It generally contains five molecules of water of crystallisation, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. It is formed by heating strong sulphuric acid with copper, sulphurous anhydride being evolved. The same salt is obtained in practice by carefully roasting sulphide ores of copper, and also by the action on them of water containing oxygen in solution : $\text{CuS} + \text{O}_4 = \text{CuSO}_4$. This salt forms a by-product, obtained in gold refineries, when the silver is precipitated from the sulphuric acid solution by means of copper. It is also obtained by pouring dilute sulphuric acid over sheet copper in the presence of air, or by heating cupric oxide or carbonate in sulphuric acid. The crystals of this salt belong to

simplest chemical relations dealing with solutions, dissociation, double decompositions, and similar cases, and therefore deserves serious consideration; but a detailed exposition of this subject must be looked for in works on physical chemistry (see also Chap. XIV., notes 24, 47, and 50; Chap. XXII., note 23, &c.).

¹⁰ The normal **cupric nitrate**, $\text{CuN}_2\text{O}_6 \cdot 3\text{H}_2\text{O}$, is obtained as a deliquescent salt of a blue colour (soluble in water and in alcohol) by dissolving copper or cupric oxide in nitric acid. It is so easily decomposed by the action of heat that it is impossible to drive off the water of crystallisation from it before it begins to decompose. During the ignition of the normal salt the cupric oxide formed enters into combination with the remaining undecomposed normal salt, and gives a basic salt, $\text{CuN}_2\text{O}_6 \cdot 2\text{CuH}_2\text{O}_2$. The same basic salt is obtained if a certain quantity of alkali or cupric hydroxide or carbonate is added to the solution of the normal salt, which is even decomposed when boiled with metallic copper, and forms the basic salt as a green powder, which easily decomposes under the action of heat and leaves a residue of cupric oxide. The basic salt, having the composition $\text{CuN}_2\text{O}_6 \cdot 3\text{CuH}_2\text{O}_2$, is nearly insoluble in water.

The normal **carbonate of copper**, CuCO_3 , occurs in nature, although extremely rarely. If solutions of cupric salts, CuX_2 , are mixed with solutions of alkali carbonates, then, as in the case of magnesium, carbonic anhydride is evolved, and basic salts are formed, which vary in composition according to the temperature and conditions of the reaction. By mixing cold solutions, a voluminous blue precipitate is formed, containing an equivalent proportion of cupric hydroxide and carbonate (after standing or heating, its composition is the same as malachite, sp. gr. 3.5) : $2\text{CuSO}_4 + 2\text{Na}_2\text{CO}_3 + \text{H}_2\text{O} = \text{CuCO}_3 \cdot \text{CuH}_2\text{O}_2 + 2\text{Na}_2\text{SO}_4 + \text{CO}_2$. If the resultant blue precipitate is heated in the liquid, it loses water and is transformed into a granular green mass of the composition Cu_2CO_3 —i.e. into a compound of the normal salt with anhydrous cupric oxide. This salt of the oxide corresponds with orthocarbonic acid, $\text{C}(\text{OH})_4 = \text{CH}_4\text{O}_4$, where 4H is replaced by 2Cu. On further boiling, this salt loses a portion of the carbonic acid, forming black cupric oxide, so unstable is the compound of copper with carbonic anhydride. Another basic salt which occurs in nature, $\text{CuH}_2\text{O}_2 \cdot 2\text{CuCO}_3$, is known as *azurite*, or blue carbonate of copper; it also loses carbonic acid when boiled with water. On mixing a solution of cupric sulphate with sodium sesquicarbonate no precipitate is at first obtained, but after boiling, a precipitate is formed having the composition of malachite. Debray obtained artificial azurite by heating cupric nitrate with chalk. Cupric chloride, CuCl_2 , crystallises with $2\text{H}_2\text{O}$ and dissolves easily in water. The addition of a larger proportion of H_2SO_4 to a strong solution of the salt causes the anhydrous CuCl_2 to separate out on cooling.

the triclinic system, have a specific gravity of 2.19, are of a beautiful blue colour, and give a solution of the same colour. A hundred parts of water at 0° dissolve 15, at 25° 23, and at 100° about 45 parts of cupric sulphate, CuSO_4 .^{10a} At 100° this salt loses a portion of its water of crystallisation, which it only parts with entirely at a high temperature (220°), and then gives a white powder of the anhydrous sulphate; and the latter, on further calcination, loses the elements of sulphuric anhydride, leaving cupric oxide, like all the cupric salts. The anhydrous (colourless) cupric sulphate is sometimes used for absorbing water: it turns blue in the process. It offers the advantage that it retains both hydrochloric acid and water, but not carbonic anhydride.¹¹ Cupric sulphate is used for steeping seed corn: this is said to prevent the growth of certain parasites on the plants. In the arts a considerable quantity of cupric sulphate is also used in the preparation of other copper salts—for instance, of certain pigments^{11a}—and a particularly

^{10a} Although sulphate of copper usually crystallises with $5\text{H}_2\text{O}$, that is, differently from the sulphates of Mg, Fe, and Mn, it is nevertheless perfectly isomorphous with them, as is seen not only in the fact that it gives isomorphous mixtures with them, containing a similar amount of water of crystallisation, but also in the ease with which it forms, like all bases analogous to MgO , double salts, $\text{R}_2\text{Cu}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ (where $\text{R} = \text{K}, \text{Rb}, \text{Cs}$), of the monoclinic system.

A detailed study of the crystalline forms of these salts, made by Tutton (1893) (see Chap. XIII., note 1), showed: (1) that 22 investigated salts of the composition $\text{R}_2\text{M}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, where $\text{R} = \text{K}, \text{Rb}, \text{Cs}$, and $\text{M} = \text{Mg}, \text{Zn}, \text{Cd}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}$, present a complete crystallographic resemblance; (2) that in all respects the Rb salts present a transition between the K and Cs salts; (3) that the Cs salts form crystals most easily, and the K salts the most difficultly, and that for the K salts of Cd and Mn it was even impossible to obtain well-formed crystals; (4) that, notwithstanding the closeness of their angles, the general appearance (habit) of the potassium compounds differs very clearly from the Cs salts, while the Rb salts present a distinct transition in this respect; (5) that the angle of inclination of one of the axes to the plane of the two other axes is least in the K salts (angle from 75° to 75° 38'), greatest in the Cs salts (from 72° 52' to 73° 50'), and in the Rb salts (from 73° 57' to 74° 42') intermediate between the two; the replacement of $\text{Mg} \dots \text{Cu}$ produces but a very small change in this angle; (6) that the other angles and the ratio of the axes of the crystals exhibit a similar variation; and (7) that the variation of the form is thus chiefly determined by the atomic weight of the alkaline metal.

¹¹ In addition to what has been said (Chap. I., note 65, and Chap. XXII., note 35) respecting the combination of CuSO_4 with water and ammonia, we may add that Lachinoff (1893) showed that $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ loses $4\frac{3}{4}\text{H}_2\text{O}$ at 180°, that $\text{CuSO}_4 \cdot 5\text{NH}_3$ also loses $4\frac{3}{4}\text{NH}_3$ at 320°, and that only $\frac{1}{4}\text{H}_2\text{O}$ and $\frac{1}{4}\text{NH}_3$ remain in combination with the CuSO_4 . The last $\frac{1}{4}\text{H}_2\text{O}$ can only be driven off by heating to 200°, and the last $\frac{1}{4}\text{NH}_3$ by heating to 360°. Ammonia displaces water from $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, but water cannot displace the ammonia from $\text{CuSO}_4 \cdot 5\text{NH}_3$.

^{11a} Commercial blue vitriol generally contains ferrous sulphate. The salt is purified by converting the ferrous salt into a ferric salt by heating the solution with chlorino or nitric acid. The solution is then evaporated to dryness, and the unchanged cupric sulphate extracted from the residue, which will contain the larger portion of the ferric oxide. The remainder will be separated if cupric hydroxide is added to the solution and the latter boiled; the cupric oxide, CuO , then precipitates the ferric oxide, Fe_2O_3 , just as it

large quantity is used in the **galvanoplastic process**, which consists in the deposition of copper from a solution of cupric sulphate by the action of a galvanic current, when the metallic copper is deposited on the cathode and takes the shape of the latter. The description of the processes of galvanoplastic art introduced by Jacobi in St. Petersburg forms a part of applied physics, and will not be touched on here, and we shall only mention that, although first introduced for small articles, it is now used for such articles as type moulds (*clichés*), for maps, prints, &c., and also for large statues, and for the deposition of iron, zinc, nickel, gold, silver, &c., on other metals and materials. The beginning of the application of the galvanic current to the practical extraction of metals from solutions has also been established, especially since the dynamo-electric machines of Gramme, Siemens, and others have rendered it possible to cheaply convert the mechanical motion of the steam engine into electric energy. It is to be expected that the application of the electric current, which has long since given such important results in chemistry, will, in the near future, play an important part in technical processes, the example being shown by electric lighting.

The alloys of copper with certain metals, and especially with zinc and tin, are easily formed by directly melting the metals together. They are easily cast into moulds, forged, and worked like copper, whilst they are much more durable in the air, and are therefore frequently used in the arts. Even the ancients used in all cases, not pure copper, but its alloys with tin or different kinds of **bronze** (Chap. XVIII., note 35 ; Chap. XV., note 19b). The alloys of copper with zinc are called **brass** or 'yellow metal.' Brass contains about 32 per cent. of zinc ; generally, however, it does not contain more than 65 per cent. of copper. The remainder is composed of lead and tin, which usually occur, although in small quantities, in brass. Yellow metal contains about 40 per cent. of zinc.¹² The addition of zinc to copper

is itself precipitated by silver oxide. But the solution will contain a small proportion of a basic salt of copper, and therefore sulphuric acid must be added to the filtered solution, and the salt allowed to crystallise. Acid salts are not formed, and cupric sulphate itself has an acid reaction on litmus paper.

¹² Among the alloys of copper resembling brass, **delta metal**, invented by A. Dick (London), is largely used (since 1883). It contains 55 per cent. of Cu, and 41 per cent. of Zn, the remaining 4 per cent. being composed of iron (as much as $3\frac{1}{2}$ per cent., which is first alloyed with zinc), or of cobalt, manganese, and certain other metals. The sp. gr. of delta metal is 8.4. It melts at 950° , and then becomes so fluid that it fills up all the cavities in a mould and forms excellent castings. It has a tensile strength of 70 kilos per sq. mm. (gun metal about 20, phosphor bronze about 30). It is very soft especially when heated to 600° ; but after forging and rolling it becomes very hard ; it is more difficultly acted upon by air and water than other kinds of brass, and preserves its golden yellow colour for any length of time, especially if well polished. It is used for

changes the colour of the latter to a considerable degree ; with a certain amount of zinc the colour of the copper becomes yellow, and with a still larger proportion of zinc, an alloy is formed which has a greenish tint. In those alloys of zinc and copper which contain a larger amount of zinc than of copper, the yellow colour disappears and is replaced by a greyish colour. But when the amount of zinc is diminished to about 18 per cent., the alloy is red and hard, and is called 'tom-bac.' A contraction takes place in alloying copper with zinc, so that the volume of the alloy is less than the sum of those of the two constituent metals. The zinc volatilises on prolonged heating at a high temperature and the excess of metallic copper remains behind. When heated in the air, the zinc oxidises before the copper, so that all the zinc alloyed with copper may be removed from the copper by this means. An important property of brass containing about 30 per cent. of zinc is that it is soft and malleable in the cold, but becomes somewhat brittle when heated. We may also mention that ordinary copper coins contain, in order to render them hard, tin, zinc, and iron ($\text{Cu}=95$ per cent.) ; that it is now customary to add a small amount of phosphorus to copper and bronze, for the same purpose ; and also that copper is added to silver and gold in coining, &c., to render it hard ; moreover, in Germany, Switzerland, and Belgium, and other countries, a silver-white alloy (melchior, German silver, &c.), for base coinage, and other purposes, is prepared from brass and nickel (from 10 to 20 per cent. of nickel ; 20 to 30 of zinc and 50 to 70 of copper), or directly from copper and nickel, or, more rarely, from an alloy containing silver, nickel, and copper.

Copper, in its cuprous compounds, is so analogous to **silver** that were there no cupric compounds, or if silver gave stable compounds of the higher oxide, AgO , the resemblance would be as close as that between chlorine and bromine, or between zinc and cadmium ; but silver compounds corresponding to AgO are quite unknown. Although silver peroxide—which was regarded as AgO , but which Berthelot (1880) recognised as the sesquioxide, Ag_2O_3 —is known, it does not form any true salts, and consequently cannot be placed along with cupric oxide. In distinction from copper, silver as a metal does not oxidise under the influence of heat ; and its oxides, Ag_2O and Ag_2O_3 , easily lose oxygen (see note 8b). Silver does **not oxidise** in

making bearings, screw propellers, valves, and many other articles. The alloys containing 45–80 per cent. of Cu crystallise in cubes if slowly cooled (Bi also gives crystals). The alloys approaching Zn_2Cu_3 in their composition exhibit the greatest resistance (under other equal conditions ; of purity, forging, rolling, &c.). The addition of 3 per cent. of Al, or 5 per cent. of Sn, improves the quality of brass. Respecting aluminium bronze, see Chap. XVII., Vol. II., p. 99.

air, and is therefore classed among the so-called **noble metals**. It has a white colour, which is much purer than that of any other known metal, especially when the metal is chemically pure. In the arts silver is always used alloyed, because chemically pure silver is so soft that it wears exceedingly easily, whilst when fused with a small amount of copper, it becomes very hard, without losing its colour.¹³

¹³ There are not many soft metals: lead, tin, copper, silver, iron, and gold are somewhat soft, and potassium and sodium very soft. The metals of the alkaline earths are sonorous and hard, and many other metals are even brittle, especially bismuth and antimony. But the very slight significance which these properties have in determining the fundamental chemical properties of substances (although, however, of immense importance in the practical applications of metals) is seen from the example shown by zinc, which is hard at the ordinary temperature, soft at 100°, and brittle at 200°. At -190° lead is sonorous.

As the value of silver depends exclusively on its purity, and as there is no possibility of telling the amount of impurities alloyed with it from its external appearance, it is customary in most countries to mark an article with the amount of pure silver it contains after an accurately made analysis known as the **assay** of the silver. In France the assay of silver shows the amount of pure silver in 1,000 parts by weight; in Russia the

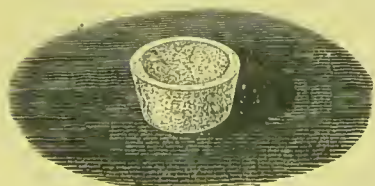


FIG. 108.—Cupel for silver assaying.

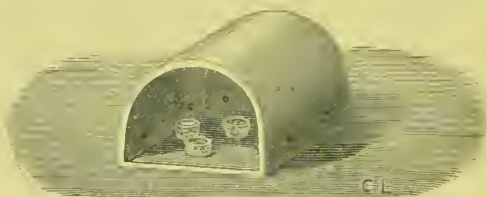


FIG. 109.—Clay muffle.

amount of pure silver in 96 parts—that is, the assay shows the number of *zolotniks* (4.26 grams) of pure silver in one pound (410 grams) of alloyed silver. Russian silver is generally 84 assay—that is, contains 84 parts by weight of pure silver and 12 parts of copper and other metals. French money contains 90 per cent. (in the Russian system this will be 86.4 assay) by weight of silver [English coins and jewellery contain 92.5 per cent. of silver]; the silver rouble is of 83½ assay—that is, it contains 86.8 per cent. of silver—and the smaller Russian silver coinage is of 48 assay, and therefore contains 50 per cent. of silver. Silver ornaments and articles are usually made in Russia of 84 and 72 assay. As the alloys of silver and copper, especially after being subjected to the action of heat, are not so white as pure silver, they generally undergo a process known as ‘blanching’ (or ‘pickling’) after being worked up. This consists in removing the copper from the surface of the article by subjecting it to a dark-red heat and then immersing it in dilute acid. During the calcination the copper on the surface is oxidised, whilst the silver remains unchanged; the dilute acid then dissolves the copper oxides formed, and pure silver is left on the surface. In order to test a silver article, a portion of its mass must be taken, not from the surface, but at a certain depth. The commonest and most often used method of assay is that known as **cupellation**. It is based on the difference in the oxidisability of copper, lead, and silver. The cupel is a porous cup with thick sides, made by compressing bone ash. The porous mass of bone ash absorbs the fused oxides, especially the lead oxide, which is easily fusible; but it does not absorb the unoxidised metal. The latter collects into a globule under the action of a strong heat in the cupel, and on cooling solidifies into a button, which may then be weighed. Several cupels are placed in a muffle. A muffle is a semi-cylindrical clay vessel, shown in the accompanying drawing. The sides of the muffle are pierced with several orifices, which allow the access of air into it. The muffle is placed in a furnace, where it is strongly

Silver occurs in **nature**, both in the free state and in certain compounds. Native silver, however, is of rather rare occurrence. A far greater quantity of silver occurs in combination with sulphur, and especially in the form of silver sulphide, Ag_2S , with lead sulphide or copper sulphide, or the ores of various other metals. The largest amount of silver is extracted from the lead in which it occurs. If this lead be calcined in the presence of air, it oxidises, and the resultant lead oxide, PbO ('litharge' or 'silberglätte,' as it is called), melts into a mobile liquid, which is easily removed. The silver remains in an unoxidised metallic state.¹⁴ This process is called 'cupellation.'

heated. Under the action of the air entering the muffle the copper of the silver alloy is oxidised; but as the oxide of copper is difficultly fusible, a certain quantity of lead is added to the alloy; the lead is also oxidised by the air at the high temperature of the muffle, and gives the very fusible lead oxide. The copper oxide then fuses with the lead oxide, and is absorbed by the cupel, whilst the silver remains as a bright white

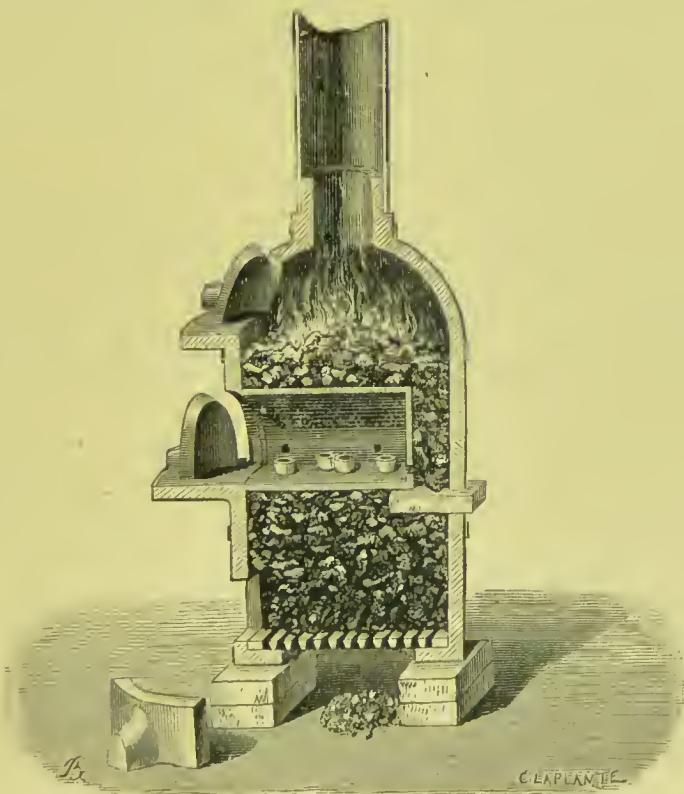


FIG. 110.—Portable muffle furnace.

globule. If the weights of the alloy taken and of the silver left on the cupel are determined, it is possible to calculate the composition of the alloy. Thus the essence of cupellation consists in the separation of the oxidisable metals from silver, which does not oxidise under the action of heat. A more accurate method, based on the precipitation of silver from its solutions in the form of silver chloride, is described in detail in works on analytical chemistry.

¹⁴ In America, whence the largest amount of silver is now obtained, ores are worked

Commercial silver generally contains copper, and, more rarely, other metallic impurities also. Chemically pure silver is obtained either by

containing not more than $\frac{1}{5}$ per cent. of silver, whilst at $\frac{1}{2}$ per cent. its extraction is very profitable. Moreover, the extraction of silver from ores containing not more than 0.01 per cent. of this metal is sometimes profitable. The majority of the lead smelted from galena contains silver, which is extracted from it. In every case the lead is first extracted in the manner described in Chapter XVIII., and this lead will contain all the silver. Not infrequently other ores of silver are mixed with lead ores in order to obtain an argentiferous lead as the product. The extraction of small quantities of silver from lead is facilitated by the fact (**Pattinson's process**) that molten argentiferous lead in cooling first deposits crystals of pure lead, which fall to the bottom of the cooling vessel, whilst the proportion of silver in the unsolidified mass increases owing to the removal of the crystals of lead (this resembles the separation of ice from salt water). The lead is enriched in this manner until it contains $\frac{1}{400}$ part of silver, and is then subjected to cupellation on a larger scale. According to Parkes's process, zinc is added to the molten argentiferous lead, and the alloy of Pb and Zn, which first separates out on cooling, is collected. This alloy is found to contain all the silver previously contained in the lead. The addition of 0.5 per cent. of aluminium to the zinc (Rossler and Edelman) facilitates the extraction of the Ag from the resultant alloy, besides preventing oxidation; for, after re-melting, nearly all the lead easily runs off (remains fluid), and leaves an alloy containing about 30 per cent. of Ag and about 70 of Zn. This alloy may be used as an anode in a solution of ZnCl_2 when the Zn is deposited on the cathode, leaving the silver with a small amount of Pb, &c., behind. The silver can be easily obtained pure by treating it with dilute acids and cupelling.

The ores of silver which contain a larger amount of it are: silver glance, Ag_2S (sp. gr. 7.2); argentiferous copper glance, CuAgS ; horn silver or chloride of silver, AgCl ; argentiferous grey copper ore; red silver ore, Ag_3SbS_3 ; polybasite, M_3RS_3 (where $\text{M} = \text{Ag}$, Cu , and $\text{R} = \text{Sb}$, As), and argentiferous gold. The latter is the usual form in which gold is found in alluvial deposits and ores. The crystals of gold from the Berezhofsky mines in the Urals contain 90 to 95 of gold and 5 to 9 of silver, and the Altai gold contains 50 to 65 of gold and 36 to 38 of silver. The proportion of silver in native gold varies between these limits in other localities. Silver ores, which generally occur in veins, usually contain native silver and various sulphur compounds. The most famous mines in Europe are in Saxony (Freiberg), which has a yearly output of as much as 26 tons of silver, Hungary and Bohemia (41 tons). In Russia, silver is extracted in the Altai and at Nerchinsk (17 tons). The richest silver mines known are in America, especially in Chili (as much as 70 tons), Mexico (200 tons), and more particularly in the Western States of North America. The richness of these mines may be judged from the fact that one mine in the State of Nevada (Comstock, near Washoe, and the cities of Gold Hill and Virginia), which was discovered in 1859, gave an output of 400 tons in 1866. In place of cupellation, chlorination may also be employed for extracting silver from its ores. The method of chlorination consists in converting the silver in an ore into silver chloride. This is done either by a wet method or by a dry method, in which the ore is roasted with NaCl . When the silver chloride is formed, the extraction of the metal is also done by two methods. The first consists in the silver chloride being reduced to metal by means of iron in rotating barrels, with the subsequent addition of mercury, which dissolves the silver but does not act on the other metals. The mercury holding the silver in solution is distilled, when the silver remains behind. This method is called **amalgamation**. The other method is less frequently used, and consists in dissolving the silver chloride in sodium chloride or in sodium thiosulphate, and then precipitating the silver from the solution. The amalgamation is then carried on in rotating barrels containing the roasted ore mixed with water, iron, and mercury. The iron reduces the silver chloride by taking up the chlorine from it. The technical details of these processes are described in works on metallurgy. The extraction of AgCl by the wet method is carried on (Patera's process) by means of a solution of hyposulphite of sodium, which dissolves AgCl (see note 23), or

cupellation or by subjecting ordinary silver to the following treatment. The silver is first dissolved in nitric acid, which converts it and the copper into nitrates, $\text{Cu}(\text{NO}_3)_2$ and AgNO_3 ; hydrochloric acid is then added to the resultant solution (green, owing to the presence of the cupric salt), which is considerably diluted, with water in order to retain the lead chloride in solution if the silver contained lead. The copper and many other metals remain in solution, whilst the silver is precipitated as silver chloride. The precipitate is allowed to settle, and the liquid is decanted off; the precipitate is then washed and fused with sodium carbonate. A double decomposition then takes place, sodium chloride and silver carbonate being formed; but the latter decomposes into metallic silver, because the silver oxide is decomposed by heat: $\text{Ag}_2\text{CO}_3 = \text{Ag}_2 + \text{O} + \text{CO}_2$. The silver chloride may also be mixed with metallic zinc, sulphuric acid, and water, and left for some time, when the zinc removes the chlorine from the silver chloride and precipitates the silver as a powder. This finely divided silver is called 'molecular silver.'¹⁵

Chemically pure silver has an exceedingly pure white colour, and a specific gravity of 10.5. Solid silver is lighter than the molten metal, and therefore a piece of silver floats on the latter. The fusing-point of silver is about 950°C ., and at the high temperature attained by the combustion of detonating gas it volatilises.¹⁶ By employing silver reduced from silver chloride by milk sugar and caustic potash, and distilling it, Stas obtained silver purer than that obtained by any other means; in fact, this was perfectly pure silver. The vapour of

by lixiviating with a 2 per cent. solution of a double hyposulphite of Na and Cu (obtained by adding CuSO_4 to $\text{Na}_2\text{S}_2\text{O}_3$). The resultant solution of AgCl is first treated with soda to precipitate PbCO_3 , and then with Na_2S , which precipitates the Ag and Au.

¹⁵ There is another practical method which is suitable for separating the silver from the solutions obtained in photography, consisting in precipitating the silver by oxalic acid. In this case the amount of silver in the solution must be known, and 23 grams of oxalic acid dissolved in 400 grams of water must be added for every 60 grams of silver in a litre of solution. A precipitate of silver oxalate, $\text{Ag}_2\text{C}_2\text{O}_4$, is then obtained, which is insoluble in water but soluble in acids. Hence, if the liquid contains any free acid it must be previously neutralised with soda. The resultant precipitate of silver oxalate is dried, mixed with an equal weight of dry sodium carbonate, and thrown into a gently heated crucible. The separation of the silver then proceeds without an explosion, whilst the silver oxalate if heated alone decomposes with explosion.

According to Stas, the best method for obtaining silver from its solutions is by the reduction of silver chloride dissolved in ammonia by means of an ammoniacal solution of cuprous thiosulphate; the silver is then precipitated in a crystalline form. A solution of ammonium sulphite may be used instead of the cuprous salt.

¹⁶ Silver is very malleable and ductile: it may be beaten into leaves 0.002 mm. in thickness. Silver wire may be made so fine that 1 gram is drawn into a wire $2\frac{1}{2}$ kilometres long. In this respect silver is second only to gold. A wire of 2 mm. diameter breaks under a strain of 20 kilograms.

silver has a very beautiful green colour, which is seen when a silver wire is placed in an oxyhydrogen flame.¹⁷

It has long been known (Wöhler) that when nitrate of silver, AgNO_3 , reacts as an oxidising agent upon citrates and tartrates, it is able under certain conditions to give either a salt of suboxide of silver (see note 19) or a red solution, or to give a precipitate of metallic silver reduced at the expense of the organic substances. In 1889 Carey Lea, in his researches on this class of reactions, showed that soluble silver is here formed, which he called *allotropic silver*. It may be obtained by taking 200 c.c. of a 10 per cent. solution of AgNO_3 and quickly adding a mixture (neutralised with NaHO) of 200 c.c. of a 30 per cent. solution of FeSO_4 and 200 c.c. of a 40 per cent. solution of sodium citrate. A lilac precipitate is obtained, which is collected on a filter (the precipitate becomes blue) and washed with a solution of NH_4NO_3 . It then becomes soluble in pure water, forming a red, perfectly transparent^{17a} solution from which the dissolved silver is precipitated on the addition of many soluble foreign bodies. Some of the latter—for instance, NH_4NO_3 , alkaline sulphates, nitrates, and citrates—give a precipitate which redissolves in pure water, whilst others—for instance, MgSO_4 , FeSO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, AgNO_3 , $\text{Ba}(\text{NO}_3)_2$, and many others—convert the precipitated silver into a new variety, which, although no longer soluble in water, regains its solubility in a solution of borax and is soluble in ammonia. Both the soluble and the insoluble silver

¹⁷ In melting, silver **absorbs** a considerable amount of **oxygen**, which is disengaged on solidifying. One volume of molten silver absorbs as much as 22 volumes of oxygen. In solidifying, the silver forms prominences and throws off metal, owing to the evolution of the gas. All these phenomena recall a volcano on a miniature scale (Dumas). Silver which contains a small quantity of copper or gold, &c., does not show this property of dissolving oxygen.

The absorption of oxygen by molten silver is, however, an oxidation, but it is at the same time a phenomenon of solution. One cubic centimetre of molten silver can dissolve twenty-two cubic centimetres of oxygen, which, even at 0° , only weigh 0.03 gram, whilst 1 cubic centimetre of silver weighs at least 10 grams, and therefore it is impossible to suppose that the absorption of the oxygen is attended by the formation of any definite compound of silver and oxygen (about 45 atoms of silver to 1 of oxygen) in any but a dissociated form, and this is the state in which substances in solution must be regarded (Chap. I.).

Le Chatelier showed that at 300° and under 15 atmospheres pressure, silver absorbs so much oxygen that it may be regarded as having formed the compound Ag_4O or a mixture of Ag_2 and Ag_2O . Moreover, silver oxide, Ag_2O , only decomposes at 300° under low pressures, whilst at pressures above 10 atmospheres there is no decomposition at 300° but only at 400° .

Stas showed that silver is oxidised by air in the presence of acids. V. d. Pfordten confirmed this, and showed that an acidified solution of potassium permanganate rapidly dissolves silver in the presence of air.

^{17a} Solutions of colloidal substances like soluble silver are really not perfectly transparent, as is shown by polarised light. As a matter of fact there is not much difference between emulsions and such solutions as these.

are rapidly converted into the ordinary grey-metallic variety by sulphuric acid, although nothing is given off in the reaction; the same change takes place on ignition, but in this case CO_2 is disengaged; the latter is formed from the organic substances which remain (to the amount of 3 per cent.) in the modified silver (they are not removed by soaking in alcohol or water). If the precipitated silver is slightly washed and laid in a smooth thin layer on paper or glass, it is seen that the soluble variety is red when moist, and a fine blue colour when dry, whilst the insoluble variety has a blue reflex. Besides these, under special conditions¹⁸ a golden yellow variety may be obtained, which gives a brilliant golden yellow coating on glass; but it is easily converted into the ordinary

¹⁸ When solutions of AgNO_3 , FeSO_4 , sodium citrate, and NaHO are mixed together in the manner described above, they throw down a precipitate of a beautiful lilac colour; when transferred to a filter paper the precipitate soon changes colour, and becomes dark blue. To obtain the substance as pure as possible it is washed with a 5–10 per cent. solution of ammonium nitrate; the liquid is decanted, and 150 c.c. of water poured over the precipitate. It then dissolves entirely in the water. A small quantity of a saturated solution of ammonium nitrate is added to the solution, and the silver in solution again separates out as a precipitate. These alternate solutions and precipitations are repeated seven or eight times, after which the precipitate is transferred to a filter and washed with 95 per cent. alcohol until the filtrate gives no residue on evaporation. An analysis of the substance so obtained showed that it contained from 97.18 to 97.31 per cent. of metallic silver. Among other methods of preparing soluble silver given by Carey Lea, we may mention the method published by him in 1891. AgNO_3 is added to a solution of dextrine in caustic soda or potash; at first a precipitate of brown oxide of silver is thrown down, but the brown colour then changes into a reddish chocolate, owing to the reduction of the silver by the dextrine, and the solution turns a deep red. A few drops of this solution turn water bright red, and give a perfectly transparent liquid. The dextrine solution is prepared by dissolving 40 grams of caustic soda and the same amount of ordinary brown dextrine, in two litres of water. To this solution is gradually added 28 grams of AgNO_3 dissolved in a small quantity of water. Many methods were subsequently discovered for preparing the soluble variety of silver and some other metals by the action of different reducing agents. Among these, hydrate of hydrazine (Chap. VI., note 22a) is distinguished for the simplicity and clearness of its action, and was employed for this purpose by Gutbier (1902).

The red solution, described above, after standing several weeks, deposits crystals spontaneously in the form of short black needles and thin prisms, the liquid becoming colourless. This insoluble variety, when rubbed upon paper, has the appearance of bright shining green flakes, which polarise light.

Carey Lea also obtained a golden variety of silver. A solution is prepared containing 200 c.c. of a 10 per cent. solution of nitrate of silver, 200 c.c. of a 20 per cent. solution of Rochelle salt, and 800 c.c. of water. Just as in the previous case the reaction consisted in the reduction of the citrate of silver, so in this case it consists in the reduction of the tartrate, which here first forms a red and then a black precipitate of allotropic Ag, which, when transferred to the filter, appears of a beautiful bronze colour. After washing and drying, this precipitate acquires the lustre and colour peculiar to polished gold, and this is especially remarked where the precipitate comes into contact with glass or china. An analysis of the golden variety gave a percentage composition of 98.750 to 98.749 Ag. Both the insoluble varieties (the blue and the gold) have a different specific gravity from ordinary silver. Whilst that of fused silver is 10.50, and that of finely divided silver 10.62, the specific gravity of the blue insoluble variety is 9.58, and

grey metallic state by friction or trituration. There is no doubt^{15a} but that there is the same relation between ordinary silver which is perfectly insoluble in water and the varieties of silver obtained by Carey Lea^{15b} as there is between quartz and soluble silica or between CuS and As₂S₃ in their ordinary insoluble forms and in the colloidal solutions of their hydrosols (see Chap. I., note 57, and Chap. XVII., note 25a). Here, however, an important step in advance has been made in this respect, that we are dealing with the solution of a simple body, and, moreover, of a metal, i.e., of a particularly characteristic state of matter. And as selenium, boron, gold, and certain other simple bodies have already been obtained in a soluble (colloid) form, and as numerous organic compounds (albuminous substances, gum, cellulose, starch, &c.) and inorganic substances are also known in this form, it might be said that the colloid state (of hydrogels and hydrosols) can be acquired, if not by every substance, at all events by substances of most varied chemical character under particular conditions of their formation from solutions. And this being the case, we may hope that a further study of soluble colloidal compounds, which apparently present various transitions towards emulsions, may throw a new light upon the complex question of solutions, which forms one of the problems of the present epoch of chemical science. Moreover, we may remark that Spring (1890) clearly proved the colloidal state of soluble silver by means of dialysis, as it did not pass through the membrane.

As regards the capacity of silver for chemical reactions, it is remarkable for its small capacity for combination with oxygen and for its considerable energy of combination with sulphur, iodine, and cer-

that of the gold variety 8.51. The gold variety passes into ordinary Ag with great ease. This transition may even be remarked on the filter in those places which have accidentally not been moistened with water.

The soluble variety of Ag also passes into the ordinary state with great ease, the heat of conversion being, as Prange showed in 1890, about +60 calories.

^{15a} The opinion of the nature of soluble silver given in the text was first enunciated in the *Journal of the Russian Chemical Society*, February 1, 1890, Vol. XXII., page 73. This view is at the present time generally accepted, and this silver is frequently known as the 'colloidal' variety. I may add that Carey Lea observed the solution of ordinary molecular silver in ammonia without the access of air.

^{15b} It is, however, noteworthy that ordinary metallic lead has long been considered soluble in water, that boron has been repeatedly obtained in a brown solution, and that observations upon the development of certain bacteria have shown that the latter die in water which has been for some time in contact with metals. This seems to indicate the passage of small quantities of metals into water (the formation of peroxide of hydrogen may, however, be supposed to have some influence in these cases). And as the colloidal state is shown chiefly by very complex molecules, the cause of the conversion of silver and other simple bodies may perhaps be explained as an aggregation of molecules. Questions of this kind, I think, are awaiting their solution by modern science, although they are unfortunately difficult and have been little studied.

tain kindred non-metals. **Silver does not oxidise** at any temperature, and its oxide, Ag_2O , is decomposed by heat. It is also a very important fact that silver is not oxidised by oxygen either in the presence of alkalies, even at exceedingly high temperatures, or in the presence of acids—at least of dilute acids—which properties render it a very important metal in chemical industry for the fusion of alkalies, and also for many purposes in everyday life; for instance, for making spoons, salt-cellar, &c. Ozone, however, oxidises it. Of all **acids** nitric acid has the greatest **action** on silver. The reaction is accompanied by the formation of oxides of nitrogen and of silver nitrate, AgNO_3 , which dissolves in water and does not, therefore, hinder the further action of the acid on the metal. The halogen acids, especially hydriodic acid, act on silver, hydrogen being evolved; but this action soon stops, owing to the halogen compounds of silver being insoluble in water and only very slightly soluble in acids; they therefore preserve the remaining mass of metal from the further action of the acid. In consequence of this the action of the halogen acids is only distinctly seen with finely divided silver. Sulphuric acid acts on silver in the same manner that it does on copper, only it must be concentrated and at a higher temperature. Sulphurous anhydride, and not hydrogen, is then evolved; but there is no action at the ordinary temperature, even in the presence of air. Among the various salts, sodium chloride (in the presence of moisture, air, and carbonic acid) and potassium cyanide (in the presence of air) act on silver more decidedly than any others, converting it respectively into silver chloride and a double cyanide.

Although silver does not directly combine with oxygen, still three different degrees of combination with oxygen may be obtained indirectly from the salts of silver. They are all, however, unstable, and decompose into oxygen and metallic silver when ignited. These three oxides of silver have the following composition: **silver suboxide**, Ag_4O ,¹⁹ corresponding with the (little investigated) suboxides of the

¹⁹ **Silver suboxide**, Ag_4O (or argentous oxide), is obtained from argentic citrate by heating it to 100° in a stream of hydrogen. Water and argentous citrate are then formed, and the latter, although but slightly soluble in water, gives a reddish-brown solution of colloidal silver (note 18), and when boiled this solution becomes colourless and deposits metallic silver, the argentic salt being again formed. Wöhler, who discovered this oxide, obtained it as a black precipitate by adding potassium hydroxide to the above solution of argentous citrate. With hydrochloric acid the suboxide gives a brown compound, Ag_2Cl . Since the discovery of soluble silver the above data cannot be regarded as perfectly trustworthy; it is probable that a mixture of Ag_2 and Ag_2O was being dealt with, so that the actual existence of Ag_4O is now doubtful; but there can be no doubt as to the formation of a subchloride, Ag_2Cl (see note 25), corresponding to the suboxide. The same compound is obtained by the action of light on the higher chloride. Other acids do not combine with silver suboxide, but convert it into an argentic salt and metallic silver. In this respect cuprous oxide

alkali metals ; **silver oxide**, Ag_2O , corresponding with the oxides of the alkali metals and the ordinary salts of silver, AgX ; and **silver peroxide**, AgO ,^{19a} or, judging from Berthelot's researches, Ag_2O_3 . **Silver oxide** is obtained as a brown precipitate (which when dried does not contain water) by adding potassium hydroxide to a solution of a silver salt—for example, of silver nitrate. The precipitate formed seems, however, to be a hydroxide, AgHO , i.e., $\text{AgNO}_3 + \text{KHO} = \text{KNO}_3 + \text{AgHO}$, and the formation of the anhydrous oxide, $2\text{AgHO} = \text{Ag}_2\text{O} + \text{H}_2\text{O}$, may be compared with the formation of the anhydrous cupric oxide by the action of potassium hydroxide on hot cupric solutions. Silver hydroxide decomposes into water and silver oxide, even at low temperatures ; at least the hydroxide no longer exists at 60° , but forms the anhydrous oxide, Ag_2O .^{19b} Silver oxide is almost insoluble in water ; but, nevertheless, it is undoubtedly a rather powerful basic oxide, because it displaces the oxides of many metals from their soluble salts, and saturates such acids as nitric acid, forming with them neutral salts, which do not act on litmus paper.²⁰ The oxide is distinguished by its great instability when heated, so that it loses all its oxygen when slightly heated. Hydrogen reduces it at about 80° .^{2Ca} The feebleness

presents a certain resemblance to these suboxides. But copper forms a suboxide of the composition Cu_4O , which is obtained by the action of an alkaline solution of stannous oxide on cupric hydroxide, and is decomposed by acids into cupric salts and metallic copper. The problems offered by the suboxides, as well as by the peroxides, cannot be considered as fully solved.

^{19a} **Silver peroxide**, AgO or Ag_2O_3 , is obtained at the anode by the decomposition of a dilute (10 per cent.) solution of silver nitrate by the action of a galvanic current (Ritter). Brittle grey needles with a metallic lustre, which occasionally attain a somewhat considerable size, are then formed. They are insoluble in water and decompose, with the evolution of oxygen, when they are dried and heated up to 150° , and, like lead dioxide, barium peroxide, &c., their action is strongly oxidising. When treated with acids, oxygen is evolved and a salt of the oxide formed. Silver peroxide absorbs sulphurous anhydride and forms silver sulphate. Hydrochloric acid evolves chlorine ; ammonia reduces the silver, and is itself oxidised, forming water and gaseous nitrogen. Analyses of the above-mentioned crystals show that they contain silver nitrate and peroxide, and water. According to Berthelot, they possess the composition $4\text{Ag}_2\text{O}_3, 2\text{AgNO}_3, \text{H}_2\text{O}$.

^{19b} According to Carey Lea, however, oxide of silver still retains water even at 100° , and only parts with it together with the oxygen. Oxide of silver is used for colouring glass yellow.

²⁰ The reaction of Pb(OH)_2 upon AgHO in the presence of NaHO leads to the formation of a compound of the two oxides, $\text{PbO}, n\text{Ag}_2\text{O}$, from which the oxide of lead cannot be removed by alkalies (Wöhler, Leton). Wöhler, Welch, and others obtained crystalline double salts, R_2AgX_4 , by the action of strong solutions of the halogen salts of the alkaline metals, RX , upon AgX , where $\text{R} = \text{Cs}, \text{Rb}, \text{K}$.

^{20a} According to Müller, ferric oxide is reduced by hydrogen (see Chap. XXII., note 5) at 295° (into FeO ?), cupric oxide at 140° , Ni_2O_3 at 150° ; nickelous oxide, NiO , is reduced to the suboxide, Ni_2O , at 195° , and to nickel at 270° ; zinc oxide requires so high a temperature for its reduction that the glass tube in which Müller conducted the experiment did not stand the heat ; antimony oxide requires a temperature of 215° for

of the affinity of silver for oxygen is shown by the fact that silver oxide decomposes under the action of light, so that it must be kept in opaque vessels. The silver salts are colourless, and decompose when heated, leaving metallic silver if the elements of the acid are volatile.^{20b} They have a peculiar metallic taste, and are exceedingly poisonous; the majority of them are acted on by light, especially in the presence of organic substances, which are then oxidised. The alkaline carbonates give a white precipitate of silver carbonate, Ag_2CO_3 , which is insoluble in water, but soluble in ammonia and ammonium carbonate. Aqueous ammonia, added to a solution of a normal silver salt, first acts like potassium hydroxide; but the precipitate dissolves in an excess of the reagent, like the precipitate of cupric hydroxide.²¹ Silver oxalate and the halogen compounds of silver are insoluble in water; hydrochloric acid and soluble chlorides give, as already repeatedly observed, a white precipitate of silver chloride in solutions of silver salts. Potassium iodide gives a yellowish precipitate of silver iodide. Zinc separates all the silver in a metallic form from solutions of silver salts. Many other metals and reducing agents—for example, organic substances—also reduce silver from the solutions of its salts.

Silver nitrate, AgNO_3 , is known by the name of *lunar caustic* (or *lapis infernalis*): it is obtained by dissolving metallic silver in nitric acid. If the silver be impure, the resultant solution will contain a mixture of the nitrates of copper and silver. If this mixture is evaporated to dryness and the residue carefully fused at an incipient red heat, all the cupric nitrate is decomposed, whilst the greater part of the silver nitrate remains unchanged. On treating the fused mass with water the latter is dissolved, whilst the cupric

* its reduction; yellow mercuric oxide is reduced at 190° and the red oxide at 230° ; silver oxide at 85° , and platinum oxide even at the ordinary temperature.

^{20b} A silica compound, Ag_2OSiO_2 is obtained by fusing AgNO_3 with silica. This salt is able to decompose with the evolution of oxygen, leaving $\text{Ag} + \text{SiO}_2$.

²¹ If a solution of a silver salt is precipitated by sodium hydroxide, and aqueous ammonia added drop by drop until the precipitate is completely dissolved, the liquid when evaporated deposits a violent mass of crystalline silver oxide. If moist silver oxide is left in a strong solution of ammonia it gives a black mass, which easily decomposes with a loud explosion, especially when struck. This black substance is called **fulminating silver**. Probably this is a compound like the other compounds of oxides with ammonia, and in exploding, the oxygen of the silver oxide forms water with the hydrogen of the ammonia, which is naturally accompanied by the evolution of heat and formation of gaseous nitrogen, or else, as Raschig states, fulminating silver contains NAg_3 or one of the amides (for instance, $\text{NHAg}_2 = \text{NH}_3 + \text{Ag}_2\text{O} - \text{H}_2\text{O}$). Fulminating silver is also formed when potassium hydroxide is added to a solution of silver nitrate in ammonia. The dangerous explosions which are produced by this compound render it needful that great care be taken when salts of silver come into contact with ammonia and alkalis (see Chap. XVI., note 26).

oxide remains insoluble. If a certain amount of silver oxide is added to the solution containing the nitrates of silver and copper, it displaces all the cupric oxide. In this case it is of course not necessary to take pure silver oxide, but only to pour off some of the solution and to add potassium hydroxide to one portion, and to mix the resultant precipitate of the hydroxides, $\text{Cu}(\text{OH})_2$ and AgOH , with the remaining portion.²² By these methods all the copper can be easily removed and pure silver nitrate obtained (its solution is colourless, while the presence of Cu renders it blue), which may be ultimately purified by crystallisation. It crystallises in colourless, transparent prismatic plates, which are not acted on by air. They are anhydrous. Its sp. gr. is 4.34 and it dissolves in half its weight of water at the ordinary temperature.^{22a} The pure salt is not acted on by light, but it easily acts in an oxidising

²² So that we here encounter the following phenomena: Copper displaces silver from the solutions of its salts, and silver oxide displaces copper oxide from cupric salts. Guided by the conceptions enunciated in Chap. XV., we can account for this in the following manner: The atomic volume of silver is 10.3, and that of copper 7.2, of silver oxide 32, and of copper oxide 13. A greater contraction has taken place in the formation of cupric oxide, CuO , than in the formation of silver oxide, Ag_2O , since in the CuO ($13 - 7 = 6$) the volume after combination with the oxygen has increased by very little, whilst the volume of silver oxide is considerably greater than that of the metal it contains [$32 - (2 \times 10.3) = 11.4$]. Hence silver oxide is less compact than cupric oxide, and is therefore less stable; but, on the other hand, there are greater intervals between the atoms in silver oxide than in cupric oxide, and therefore silver oxide is able to give more stable compounds than those of copper oxide. This is verified by the figures and data of their reactions. The specific gravity of copper sulphate in an anhydrous state is 3.53, and that of silver sulphate 5.36; the molecular volume of the former is 45, and of the latter 58. The group SO_3 in the copper occupies, as it were, a volume $45 - 13 = 32$, and in the silver salt a volume $58 - 32 = 26$; hence a smaller contraction has taken place in the formation of the copper salt from the oxide than in the formation of the silver salt, and consequently the latter should be more stable than the former. Hence silver oxide is able to decompose the salt of copper oxide, whilst with respect to the metals both salts have been formed with an almost identical contraction, since 58 volumes of the silver salt contain 21 volumes of metal (difference = 37), and 45 volumes of the copper salt contain 7 volumes of copper (difference = 38). Besides which it must be observed that copper oxide displaces iron oxide, just as silver oxide displaces copper oxide. Silver, copper, and iron, in the form of oxides, displace each other in the above order, but in the form of metals in the reverse order (iron, copper, silver). The cause of this order of the displacement of the oxides lies, amongst other things, in their composition. They have the compositions Ag_2O , Cu_2O , Fe_2O_3 ; the oxide containing a less proportion of oxygen displaces that containing a larger proportion, because the basic character diminishes with the increase of contained oxygen.

Copper also displaces mercury from its salts. It may here be remarked that Spring (1888), on leaving a mixture of dry mercurous chloride and copper for two hours, observed a distinct reduction, which belongs to the category of those phenomena which demonstrate the existence of a mobility of parts (i.e., atoms and molecules) in solid substances.

^{22a} The solution of 1 part by weight of AgNO_3 requires (according to Kremers) the following amounts of water: At 0° , 0.82 part, at 19.5° , 0.41 part, at 54° , 0.20 part, at 110° , 0.09 part, and, according to Tilden, at 125° , 0.0617 part, and at 133° , 0.0515 part.

manner on the majority of organic substances, which it generally blackens. This is due to the fact that the organic substance is oxidised by the silver nitrate, which is reduced to metallic silver. The latter is thus obtained in a finely divided state, which causes the black stain. This peculiarity is taken advantage of for marking linen. Silver nitrate is for the same reason used **for cauterising wounds** and various growths on the body. Here, again, it acts by virtue of its oxidising capacity in destroying the organic matter, which it oxidises, as is seen from the separation of a coating of black metallic powdery silver on the part cauterised.^{22b} From the description of the preparation of silver nitrate it will have been seen that this salt, which fuses at 218° , does not decompose at an incipient red heat; when cast into sticks it is usually employed for cauterising. On further heating, the fused salt undergoes decomposition, forming first silver nitrite and then metallic silver. With ammonia, silver nitrate forms, on evaporation of the solution, colourless crystals containing $\text{AgNO}_3 \cdot 2\text{NH}_3$ (Marignac). In general the salts of silver, like cuprous, cupric, zinc, &c., salts, are able to give several compounds with ammonia; for example, silver nitrate in a dry state absorbs three molecules (Rose). The ammonia is generally easily expelled from these compounds by the action of heat.

Nitrate of silver readily forms double salts like $\text{AgNO}_3 \cdot 2\text{NaNO}_3$, and $\text{AgNO}_3 \cdot \text{KNO}_3$. Under the action of water and a halogen silver nitrate gives nitric acid (see Vol. I., p. 299, formation of N_2O_5), a halogen salt of silver, and a silver salt of an oxygen acid of the halogen. Thus, for example, a solution of chlorine in water, when mixed with a solution of silver nitrate, gives silver chloride and chlorate. It is here evident that the reaction of the silver nitrate is identical with the reaction of the caustic alkalis, as the nitric acid is all set free and the silver oxide only reacts in exactly the same way as aqueous potash acts on free chlorine. Hence the reaction may be expressed in the following manner:

$$6\text{AgNO}_3 + 3\text{Cl}_2 + 3\text{H}_2\text{O} = 5\text{AgCl} + \text{AgClO}_3 + 6\text{HNO}_3.$$

Silver nitrate, like the nitrates of the alkalis, does not contain any water of crystallisation. Moreover, the other salts of silver almost always separate out without any water of crystallisation. The silver salts are further characterised by the fact that they **give neither basic nor acid salts**, owing to which the formation of silver salts generally forms the means of determining the true composition of acids; thus, to any acid H_nX there corresponds a salt Ag_nX —for instance, Ag_3PO_4 (Chap. XIX., note 15).

^{22b} It may be remarked that the black stain produced by the reduction of metallic silver disappears under the action of a solution of mercuric chloride or of potassium cyanide, because these salts act on finely divided silver.

Silver gives insoluble and exceedingly stable compounds with the halogens. They are obtained by double decomposition with great facility whenever a silver salt comes into contact with halogen salts. Solutions of nitrate, sulphate, and all other kindred salts of silver give a precipitate of silver chloride or iodide with solutions of chlorides and iodides and of the halogen acids, because the halogen salts of silver are insoluble both in water²³ and in other acids. Silver chloride, AgCl , is then obtained as a white flocculent precipitate, silver bromide forms a yellowish precipitate, and silver iodide has a very distinct yellow colour. These halogen compounds sometimes occur in nature: they are formed by a dry method—by the action of halogen compounds on silver compounds, especially under the influence of heat. Silver chloride easily fuses at 451° . On cooling from a molten state, it forms a somewhat soft hornlike mass which can be cut with a knife and is known as **horn silver**. It volatilises at a higher temperature. Its ammoniacal solution, on the evaporation of the ammonia, deposits crystalline chloride of silver, in octahedra. Bromide and iodide of silver also appear in forms of the regular system, so that in this respect the halogen salts of silver resemble the halogen salts of the alkali metals.²⁴

²³ Silver chloride is almost completely insoluble in water, but is somewhat soluble in water containing sodium chloride or hydrochloric acid, or other chlorides, and many salts, in solution. Thus at 100° , 100 parts of water saturated with sodium chloride dissolve 0.4 part of silver chloride. Bromide and iodide of silver are less soluble in this respect, as also in regard to other solvents. It should be remarked that silver chloride dissolves in solutions of ammonia, potassium cyanide, and sodium thiosulphate, $\text{Na}_2\text{S}_2\text{O}_3$. Silver bromide is almost perfectly analogous to the chloride, but silver iodide is nearly insoluble in a solution of ammonia. Silver chloride even absorbs dry ammonia gas, forming very unstable ammoniacal compounds. When heated, these compounds (Chap. VI., note 8) evolve the ammonia, as they also do under the action of all acids. Silver chloride enters into double decomposition with potassium cyanide, forming a soluble double cyanide, which we shall presently describe. It also forms a soluble double salt, NaAgS_2O_3 , with sodium thiosulphate.

Silver chloride offers different modifications in the structure of its molecule, as is seen in the variations in the consistency of the precipitate, and in the differences in the action of light, which partially decomposes AgCl (see note 25). Stas and Carey Lea investigated this subject, which has a particular importance in photography, because silver bromide also gives *photo-salts*. There is still much to be discovered in this respect, since Abney showed that perfectly dry AgCl placed in a vacuum in the dark is not in the least acted upon when subsequently exposed to light.

²⁴ Silver bromide and iodide (which occur as the minerals bromite and iodite) resemble the chloride in many respects, but the degree of affinity of silver for iodine is greater than that for chlorine and bromine, although less heat is evolved (see note 28a). Deville deduced this fact from a number of experiments. Thus silver chloride, when treated with hydriodic acid, evolves hydrochloric acid, and forms silver iodide. Finely divided silver easily liberates hydrogen when treated with hydriodic acid, and also produces the same decomposition with hydrochloric acid, but in a considerably less degree and only on the surface. The difference between silver chloride and iodide is especially remarkable, since the formation of the former is attended with a greater contraction

Silver chloride may be decomposed, with the separation of silver oxide, by heating it with a solution of an alkali, and if an organic

than that of the latter. The volume of AgCl is 26, of chlorine 27, of silver 10, the sum being 37, so that a contraction has ensued; and in the formation of silver iodide an expansion takes place, for the volumes of Ag and I are 10 and 26 respectively, and that of AgI 39 instead of 36 (density, AgCl, 5.59; AgI, 5.67). The atoms of chlorine have united with the atoms of silver without moving asunder, whilst the atoms of iodine must have moved apart in combining with the silver. It is otherwise with respect to the metal; the distance between its atoms in the metal is 2.2, in silver chloride 3.0, and in silver iodide 3.5; hence its atoms have moved asunder considerably in both cases. It is also very remarkable, as Fizeau observed, that the density of silver iodide increases with a rise of temperature—that is, a contraction takes place when it is heated and an expansion when it is cooled.

In order to explain the fact that in silver compounds the iodide is more stable than the chloride and oxide, Professor N. N. Beketoff, in his *Researches on the Phenomena of Substitutions* (Kharkoff, 1865), proposed the following original hypothesis, which we shall give in almost the words of the author:—In the case of aluminium, the oxide, Al_2O_3 , is more stable than the chloride, Al_2Cl_3 , or the iodide, AlI_3 . In the oxide the amount of the metal is to the amount of the element combined with it as 54.8 ($\text{Al}=27.3$) is to 48, or in the ratio 112 : 100; for the chloride the ratio is 25 : 100; and for the iodide, 7 : 100. In the case of silver the oxide (ratio=1350 : 100) is less stable than the chloride (ratio=304 : 100), and the iodide (ratio of the weight of metal to the weight of the halogen = 85 : 100) is the most stable. From these and similar examples it follows that the most stable compounds are those in which the weights of the combined substances are equal. This may be partly explained by the attraction of similar molecules even after they have passed into combination with others. This attraction is proportional to the product of the acting masses. In silver oxide the attraction of Ag_2 for $\text{Ag}_2=216 \times 216=46656$, and the attraction of Ag_2 for $\text{O}=216 \times 16=3456$. The attraction of like molecules thus counteracts the attraction of the unlike molecules. The former naturally does not overcome the latter, otherwise there would be a disruption, but it nevertheless diminishes the stability. In the case of an equality or proximity of the magnitude of the combining masses, the attraction of the like parts will counteract the stability of the compound to the least extent; in other words, with an inequality of the combined masses the molecules have an inclination to return to an elementary state, to decompose, which does not exist to such an extent where the combined masses are equal. There is, therefore, a tendency for large masses to combine with large ones, and for small to combine with small ones. Hence $\text{Ag}_2\text{O} + 2\text{KI}$ gives $\text{K}_2\text{O} + 2\text{AgI}$. The influence of an equality of masses on the stability is seen particularly clearly in the effect of a rise of temperature. Argentine, mercuric, auric, and other oxides, composed of unequal masses, are somewhat readily decomposed by heat, whilst the oxides of the lighter metals (like water) are not so easily decomposed. Silver chloride and iodide approach the condition of equality, and are not decomposed by heat. The most stable oxides under the action of heat are those of magnesium, calcium, silicon, and aluminium, since they also approach the condition of equality. For the same reason hydriodic acid decomposes with greater facility than hydrochloric acid. Chlorine does not act on magnesia or alumina, but it acts on lime and silver oxide, &c. This is partially explained by the fact that by considering heat as a mode of motion, and knowing that the atomic heats of the free elements are equal, it must be supposed that the amount of the motion of atoms (their *vis viva*) is constant; and as it is equal to the product of the mass (atomic weight) into the square of the velocity, it follows that the greater the combining weight the smaller will be the square of the velocity; and if the combining weights be nearly equal, the velocities also will be nearly equal. Hence the greater the difference between the weights of the combined atoms the greater will be the difference between their velocities. The difference between the velocities will increase with the temperature, and therefore the temperature of decomposition will be the sooner obtained the greater the original difference—that is,

substance is added to the alkali, the chloride can be easily reduced to metallic silver, the silver oxide being reduced in the oxidation of the organic substance. Iron, zinc, and many other metals reduce silver chloride in the presence of water. Cuprous and mercurous chlorides and many organic substances are also able to reduce the silver from chloride of silver. Silver iodide is much more stable than the chloride. The same is also observed with respect to the **action of light** upon moist AgCl . White silver chloride soon acquires a violet colour when exposed to the action of light, and especially under the direct action of the sun's rays. After being acted upon by light it is no longer entirely soluble in ammonia, but leaves metallic silver undissolved, from which it might be assumed that the action of light consisted in the decomposition of the silver chloride into chlorine and metallic silver, and in fact the silver chloride becomes in time darker and darker. Silver bromide and iodide are much more slowly acted on by light, and, according to certain observations, when pure they are even quite unacted on; at least they do not change in weight, so that if they are acted on by light, the change they undergo must be one of a change in the structure of their parts, and not of decomposition, as it is in silver chloride.^{24a} The silver chloride under the action of light changes in weight, indicating the formation of a volatile product, and the deposition of metallic silver on dissolving in ammonia shows the loss of chlorine. The change does actually occur under the action of light, but the decomposition does not go as far as into chlorine and silver, but only to the formation of a subchloride of silver, Ag_2Cl ,

the greater the difference of the weights of the combined substances. The nearer these weights are to each other, the more analogous the motion of the unlike atoms, and, consequently, the more stable the resultant compound.

The instability of cupric chloride and nitric oxide, the absence of compounds of fluorine with oxygen, whilst there are compounds of oxygen with chlorine, the greater stability of the oxygen compounds of iodine than those of chlorine, the stability of boron nitride, and the instability of cyanogen, and a number of similar instances, where, judging from the above argument, one would expect (owing to the closeness of the atomic weights) a stability, show that Beketoff's addition to the mechanical theory of chemical phenomena is still far from sufficient to explain the true relations of affinities. Nevertheless, in his mode of explaining the relative stabilities of compounds, we find an exceedingly interesting treatment of questions of primary importance. Without such efforts it would be impossible to generalise the complex data of experimental knowledge.

Fluoride of silver, AgF , is obtained by dissolving Ag_2O or Ag_2CO_3 in hydrofluoric acid. It differs from the other halogen salts of silver in being soluble in water (1 part of salt in 0.55 of water). It crystallises from its solution in prisms, $\text{AgF} \cdot \text{H}_2\text{O}$ (Marignac), or $\text{AgF} \cdot 2\text{H}_2\text{O}$ (Pfaundler), which lose their water *in vacuo*. Giintz (1891), by electrolysis a saturated solution of Ag_2F , obtained *subfluoride of silver*, Ag_2F , which is decomposed by water into $\text{AgF} + \text{Ag}$. It is also formed by the action of a strong solution of AgF upon finely divided (precipitated) silver.

^{24a} The bromogelatine photographic plates now used probably contain the halogen salts of silver in a special colloidal state, as is indicated by what is said in note 25a.

which is of a brown colour, and is easily decomposed into metallic silver and silver chloride, $\text{Ag}_2\text{Cl} = \text{AgCl} + \text{Ag}$. This change of the chemical composition and structure of the halogen salts of silver, under the action of light forms the basis of **photography**, because the halogen compounds of silver, after having been exposed to light, give a precipitate of finely divided silver, of a black colour, when treated with reducing agents.²⁵

²⁵ In photography these are called 'developers.' The most common developers are: solutions of ferrous sulphate, pyrogallol, ferrous oxalate, hydroxylamine, potassium sulphite, hydroquinone (the last acts particularly well and is very convenient to use), &c. The chemical processes of photography are of great practical and theoretical interest, but it would be impossible in this work to enter into this special branch of chemistry, which has as yet been very little worked out from a theoretical point of view. Nevertheless we shall pause to consider certain aspects of this subject which are of a purely chemical interest, and especially the facts concerning **subchloride of silver**, Ag_2Cl (see note 19), and the *photo-salts* (note 23). There is no doubt that under the action of light AgCl becomes darker in colour, decreases in weight, and probably forms a mixture of AgCl , Ag_2Cl , and Ag . But the isolation of the subchloride has only been recently accomplished by Güntz by means of the Ag_2F , discovered by him (see note 24). Many chemists (and among them Hodgkinson) assumed that an oxychloride of silver was formed by the decomposition of AgCl under the action of light. Carey Lea's (1889) and A. Richardson's (1891) experiments showed that the product formed does not, however, contain any oxygen at all, and the change in colour produced by the action of light upon AgCl is most probably due to the formation of Ag_2Cl . This substance was isolated by Güntz (1891) by passing HCl over crystals of Ag_2F (note 24). He also obtained Ag_2I in a similar manner by passing HI , and Ag_2S by passing H_2S over Ag_2F . Ag_2Cl is best prepared by the action of phosphorus trichloride upon Ag_2F . Ag_2Cl has an easily changeable tint, with shades of violet red to violet black. Under the action of light, a similar (isomeric) substance is obtained, which splits up into $\text{AgCl} + \text{Ag}$ when heated. With potassium cyanide, Ag_2Cl gives $\text{Ag} + \text{AgCN} + \text{KCl}$, whence it is possible to calculate the heat of formation of Ag_2Cl : it has the value 29.7, whilst the heat of formation of AgCl is 29.2, i.e., the reaction $2\text{AgCl} = \text{Ag}_2\text{Cl} + \text{Cl}$ corresponds to an absorption of 28.7 major calories. If we admit the formation of such a compound by the action of light, it is evident that the energy of the light is consumed in the above reaction. Carey Lea (1892) subjected AgCl , AgBr , and AgI to a pressure (of course in the dark) of 3,000 atmospheres, and to trituration with water in a mortar, and observed a change of colour indicating incipient decomposition, which is facilitated under the action of light by the molecular currents set up (Lermantoff, Egoroff). The change of colour of the halogen salts of silver under the action of light, and their faculty of subsequently giving a visible photographic image under the action of 'developers,' must now be regarded as connected with the decomposition of AgX , leading to the formation of Ag_2X , and the different tinted photo-salts must be considered as systems containing such Ag_2X 's. Carey Lea obtained photo-salts of this kind not only by the action of light but also in many other ways, which we shall enumerate to prove that they contain the products of an incomplete combination of Ag with the halogens (for the salts Ag_2X must be regarded as such). The photo-salts have been obtained (1) by the imperfect chlorination of silver; (2) by the incomplete decomposition of Ag_2O or Ag_2CO_3 by alternately heating and treating with a halogen acid; (3) by the action of nitric acid or $\text{Na}_2\text{S}_2\text{O}_3$ upon Ag_2Cl ; (4) by mixing a solution of AgNO_3 with the hydrates of FeO , MnO , and CrO , and precipitating by HCl ; (5) by the action of HCl upon the product obtained by the reduction of citrate of silver in hydrogen (note 19); and (6) by the action of milk sugar upon AgNO_3 mixed with soda and afterwards acidulating with HCl . All these reactions should lead to the formation of products of imperfect combination with the halogens and give

The insolubility of the halogen compounds of silver forms the basis of many methods used in practical chemistry. Thus, by means of this reaction, it is possible to obtain salts of other acids from a halogen salt of a given metal, for instance, $RCl_2 + 2AgNO_3 = R(NO_3)_2 + 2AgCl$. The formation of the halogen compounds of silver is very frequently used in the investigation of organic substances; for example, if any product of metalepsis containing iodine or chlorine is heated with a silver salt or silver oxide, the silver combines with the halogen and gives a halogen salt, whilst the elements previously combined with the silver replace the halogen. For instance, ethylene dibromide, $C_2H_4Br_2$, is transformed into ethylene diacetate, $C_2H_4(C_2H_3O_2)_2$, and silver bromide by heating it with silver acetate, $2C_2H_3O_2Ag$. The insolubility of the halogen compounds of silver is still more frequently taken advantage of in determining the amount of silver and halogen in a given solution. If it is required, for instance, to determine the quantity of chlorine present in the form of a metallic chloride in a given solution, a solution of silver nitrate is added to it so long as it gives a precipitate. On shaking the liquid, the silver chloride readily settles in the form of heavy flakes. It is possible in this way to precipitate the whole of the chlorine from a solution without adding an excess of silver nitrate, since it can be easily seen whether the addition of a fresh quantity of silver nitrate produces a precipitate in the clear liquid. In this manner it is possible to add to a solution containing chlorine as much silver as is required for its entire precipitation, and to calculate the amount of chlorine previously in solution from the amount of the solution of silver nitrate consumed, if the quantity of silver nitrate in this solution has been previously determined.^{25a} The atomic proportions of silver and halogen in the photo-salts of a similar diversity of colour to those produced by the action of developers upon the halogen salts of silver after exposure to light.

^{25a} In order to determine when the reaction is at an end, a few drops of a solution of K_2CrO_4 are added to the solution of the chloride. Before all the chlorine is precipitated as $AgCl$, the precipitate (after shaking) is white, since Ag_2CrO_4 with $2RCl$ gives $2AgCl$; but when all the chlorine is thrown down, Ag_2CrO_4 is formed, which colours the precipitate reddish-brown. In order to obtain accurate results the liquid should be neutral to litmus. Although distinguished by its great and frequently made use of insolubility, chloride of silver does not separate out as a visible precipitate, but remains for some time in the form of a colloidal (transparent) solution (hydrosol) when it is formed in the presence of an excess of glue or other colloidal substance (or even a strong solution of sugar, according to Lobry de Bruyn, 1902). This phenomenon is connected with a number of other phenomena—not yet sufficiently generalised—such as the solution of the metals themselves (for instance, soluble silver; see above) and their sulphides. This leads to the thought that the passage of a substance from a liquid soluble state to a solid state, or the new formation of a solid, *always*, apparently, starts from a colloidal state (of a hydrosol), which under other conditions *very quickly* passes into an insoluble crystalline form. Tammann's researches lead to such a conclusion, and questions of this kind are of great interest, and likely to be of great importance in physics and chemistry.

tions and preliminary experiments with a pure salt—for example, with sodium chloride—will give the amount of chlorine from the quantity of silver nitrate. Details of these methods will be found in works on analytical chemistry.^{25b}

^{25b} **Silver cyanide**, AgCN , is closely analogous to the haloid salts of silver. It is obtained, in similar manner to silver chloride, by the addition of potassium cyanide to silver nitrate. A white precipitate is then formed, which is almost insoluble in boiling water. It is also, like silver chloride, insoluble in dilute acids. However, it is dissolved when heated with nitric acid, and both hydriodic and hydrochloric acids act on it, converting it into silver chloride and iodide. Alkalies, however, do not act on silver cyanide, although they act on the other haloid salts of silver. Ammonia and solutions of the cyanides of the alkali metals dissolve silver cyanide, as they do the chloride. In the latter case double cyanides are formed, for example, KAgC_2N_2 . This salt is obtained in a crystalline state on evaporating a solution of silver cyanide in potassium cyanide. It is much more stable than silver cyanide itself. It has a neutral reaction, does not change in the air, and does not smell of hydrocyanic acid. Many acids, in acting on a solution of this double salt, precipitate the insoluble silver cyanide. Metallic silver dissolves in a solution of potassium cyanide in the presence of air, with formation of the same double salt and potassium hydroxide, and when silver chloride dissolves in potassium cyanide it forms potassium chloride, besides the salt KAgC_2N_2 . This double salt of silver is used in silver plating. For this purpose potassium cyanide is added to its solution, as otherwise silver cyanide, and not metallic silver, is deposited by the electric current. If two electrodes—one positive (silver) and the other negative (copper)—are immersed in such a solution, silver will be deposited upon the latter, and the silver of the positive electrode will be dissolved by the liquid, which will thus preserve the same amount of metal in solution as it originally contained. If instead of the negative electrode a copper object is taken, well cleaned from all dirt, the silver will be deposited thereon in an even coating. This, indeed, forms the mode of **silver plating by the wet method**, which is most often used in practice. A solution of one part of silver nitrate in 30 to 50 parts of water, mixed with a sufficient quantity of a solution of potassium cyanide to redissolve the precipitate of silver cyanide formed, gives a dull coating of silver; but if twice as much water is used the same mixture gives a bright coating.

Silver-plating in the wet way has now replaced to a considerable extent the old process of **dry silvering**, because this process, which consists in dissolving silver in mercury and applying the amalgam to the surface of the objects, and then vaporising the mercury, offers the great disadvantage of the poisonous nature of the mercury fumes. Besides these, there is another method of silver plating, based on the direct displacement of silver from its salts by other metals—for example, by copper. The copper reduces the silver from its compounds, and the silver separated is deposited upon the copper. Thus, a solution of silver chloride in sodium thiosulphate deposits a coating of silver upon a strip of copper immersed in it. It is best for this purpose to take pure **silver sulphite**. This is prepared by mixing a solution of silver nitrate with an excess of ammonia and adding a saturated solution of sodium sulphite and then alcohol, which precipitates silver sulphite from the solution. The sulphite and its solutions are very easily decomposed by copper. Metallic iron produces the same decomposition, and iron and steel articles may be very readily silver-plated by means of the thiosulphate solution of silver chloride. Indeed, copper and similar metals may even be silver-plated by means of silver chloride; if the chloride of silver, with a small amount of acid, is rubbed upon the surface of the copper, the latter becomes covered with a coating of silver, which it has reduced.

Silver-plating is not only applicable to metallic objects, but also to glass, china, &c. Glass is silvered for various purposes—for example, glass globes silvered internally are used for ornamentation, and have a mirrored surface. Common looking-glass silvered upon one side forms a mirror which is better than the ordinary mercury mirrors, owing

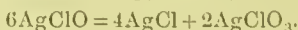
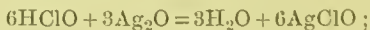
Accurate experiments, and more especially the **researches of Stas** at Brussels, show the proportion in which silver reacts with metallic chlorides. These researches have led to the determination of the **atomic or combining weights** of silver, sodium, potassium, chlorine, bromine, iodine, and other elements, and are distinguished for their model exactitude, and we shall therefore describe them in some detail. As sodium chloride is the chloride most generally used for the precipitation of silver, since it can most easily be obtained in a pure state, we shall here cite the quantitative observations made by Stas for showing the co-relation between the quantities of chloride of sodium and silver which react together. In order to obtain perfectly pure sodium chloride, he took pure rock salt, containing only a small quantity of magnesium and calcium compounds and a small amount of potassium salts. This salt was dissolved in water, and the saturated solution evaporated by boiling. The sodium chloride separated out during the boiling, and the mother liquor containing the impurities was poured off. Alcohol of 65 per cent. strength and platinic chloride were added to the resultant salt in order to precipitate all the potassium and a certain part of the sodium salts. The resultant alcoholic solution, containing the sodium and platinum chlorides, was then mixed with a solution of pure ammonium chloride in order to remove the platinic chloride. After this precipitation the solution was evaporated in a platinum retort, and then separate portions of this purified sodium chloride were collected as they crystallised. The same salt was prepared from sodium sulphate, tartrate, nitrate, and from the platini-chloride, in order to have sodium chloride prepared by different methods and from different sources, and in this manner ten samples of sodium chloride were purified and investigated in their relation to silver. After being dried, weighed quantities of all ten samples of sodium chloride were dissolved in water and mixed with a solution in nitric acid of a weighed quantity of perfectly pure silver. A slightly greater quantity of silver was taken than would be

to the truer colours of the image, due to the whiteness of the silver. For optical instruments—for example, telescopes—concave mirrors are now made of silvered glass, which has first been ground and polished into the required form. The **silvering of glass** is based on the fact that silver which is reduced from certain solutions deposits itself uniformly in a perfectly homogeneous and continuous but very thin layer, forming a bright reflecting surface. Certain organic substances have the property of reducing silver in this form. The best known among these are certain aldehydes—for instance, ordinary acetaldehyde, C_2H_5O , which easily oxidises in the air and forms acetic acid, $C_2H_4O_2$. This oxidation also easily takes place at the expense of silver oxide, when a certain amount of ammonia is added to the mixture. The oxide of silver gives up its oxygen to the aldehyde, and the silver reduced from it is deposited in a metallic state in a uniform bright coating. The same action is produced by certain saccharine substances and organic acids, such as tartaric acid, &c.

required for the decomposition of the sodium chloride, and when, after pouring in all the silver solution, the silver chloride had settled, the amount of silver remaining in excess was determined by means of a solution of sodium chloride of known strength. This solution of sodium chloride was added so long as it formed a precipitate. In this manner Stas determined how many parts of sodium chloride correspond to 100 parts by weight of silver. The result of ten determinations was that for the entire precipitation of 100 parts of silver from 54.2060 to 54.2093 parts of sodium chloride were required. The difference is so inconsiderable that it has no perceptible influence on the subsequent calculations. The mean of ten experiments was that 100 parts of silver react with 54.2078 parts of sodium chloride. In order to learn from this the relation between the chlorine and silver, it was necessary to determine the quantity of chlorine contained in 54.2078 parts of sodium chloride, or, what is the same thing, the quantity of chlorine which combines with 100 parts of silver. For this purpose Stas made a series of observations on the quantity of silver chloride obtained from 100 parts of silver. Four syntheses were made by him for this purpose. The first synthesis consisted in the formation of silver chloride by the action of chlorine on silver at a red heat. This experiment showed that 100 parts of silver give 132.841, 132.843, and 132.843 of silver chloride. The second method consisted in dissolving a given quantity of silver in nitric acid and precipitating it by means of gaseous hydrochloric acid passed over the surface of the liquid; the resultant mass was evaporated in the dark to drive off the nitric acid and the excess of hydrochloric acid, and the remaining silver chloride was fused first in an atmosphere of hydrochloric acid gas and then in air. In this process the silver chloride was not washed, and therefore there could be no loss from solution. Two experiments made by this method showed that 100 parts of silver give 132.849 and 132.846 parts of silver chloride. A third series of determinations was also made by precipitating a solution of silver nitrate with a certain excess of gaseous hydrochloric acid. The amount of silver chloride obtained was altogether 132.848. Lastly, a fourth determination was made by precipitating dissolved silver with a solution of ammonium chloride, when it was found that a considerable amount of silver (0.3175) had passed into solution in the washing; for 100 parts of silver there was obtained altogether 132.8417 of silver chloride. Thus, from the mean of seven determinations it appears that 100 parts of silver give 132.8445 parts of silver chloride—that is, that 32.8445 parts of chlorine are able to combine with 100 parts of silver and with that quantity of sodium which is contained in 54.2078 parts of sodium chloride. These observations show that 32.8445 parts of chlorine combine with 100 parts of

silver and with 21.3633 parts of sodium. From these figures, expressing the relation between the combining weights of chlorine, silver, and sodium, it would be possible to determine their atomic weights—that is, the combining quantity of these elements with respect to one part by weight of hydrogen or 16 parts of oxygen, if there existed a series of similarly accurate determinations for the reactions between hydrogen or oxygen and one of these elements—chlorine, sodium, or silver. If we determine the quantity of silver chloride which is obtained from silver chlorate, AgClO_3 , we shall find the relation between the combining weights of silver chloride and oxygen, so that, taking the quantity of oxygen as a constant magnitude, we can learn from this reaction the combining weight of silver chloride, and from the preceding numbers the combining weights of chlorine and silver. For this purpose it was first necessary to obtain pure silver chlorate. This Stas did by acting on silver oxide or carbonate, suspended in water, with gaseous chlorine.²⁵

²⁶ The phenomenon which then takes place is described by Stas as follows, in a manner which is perfect in its clearness and accuracy: if silver oxide or carbonate is suspended in water, and an excess of water saturated with chlorine added, all the silver will be converted into chloride, just as is the case with oxide or carbonate of mercury, and the water then contains, besides the excess of chlorine, only pure hypochlorous acid without the least trace of chloric or chlorous acid. If a stream of chlorine is passed into water containing *an excess of silver oxide* or silver carbonate while the liquid is continually agitated, the reaction is the same as the preceding; silver chloride and hypochlorous acid are formed. But this acid does not long remain in a free state: it gradually acts on the silver oxide and gives **silver hypochlorite**, i.e., AgClO . If, after some time, the current of chlorine is stopped but the shaking continued, the liquid loses its characteristic odour of hypochlorous acid, while preserving its energetic decolorising property, because the silver hypochlorite which is formed is easily soluble in water. In the presence of an excess of silver oxide this salt can be kept for several days without decomposition, but it is exceedingly unstable when no excess of silver oxide or carbonate is present. So long as the solution of silver hypochlorite is shaken up with the silver oxide it preserves its transparency and bleaching property; but directly it is allowed to stand, and the silver oxide settles, it becomes rapidly cloudy and deposits large flakes of silver chloride, so that the black silver oxide which had settled becomes covered with the white precipitate. The liquid then loses its bleaching properties and contains in solution **silver chlorate**, i.e., AgClO_3 , which has a slightly alkaline reaction, owing to the presence of a small amount of dissolved oxide. In this manner the reactions which are consecutively accomplished may be expressed by the equations:



Hence, Stas gives the following method for the preparation of silver chlorate: A slow current of chlorine is caused to act on oxide of silver, suspended in water which is kept in a state of continual agitation. The shaking is continued after the supply of chlorine has been stopped, in order that the free hypochlorous acid should pass into silver hypochlorite, and the resultant solution of the hypochlorite is drawn off from the sediment of the excess of silver oxide. This solution decomposes spontaneously into silver chloride and chlorate. The pure silver chlorate, AgClO_3 , does not change under the action of light. The salt is prepared for further use by drying it in dry air at 150° . It is neces-

The decomposition of the silver chlorate thus obtained was accomplished by the action of a solution of sulphurous anhydride on it. The salt was first fused by carefully heating it at 243° . The solution of sulphurous anhydride used was one saturated at 0° . Sulphurous anhydride in dilute solutions is oxidised at the expense of silver chlorate, even at low temperatures, with great ease if the liquid is continually shaken, sulphuric acid and silver chloride being formed: $\text{AgClO}_3 + 3\text{SO}_2 + 3\text{H}_2\text{O} = \text{AgCl} + 3\text{H}_2\text{SO}_4$. After decomposition, the resultant liquid was evaporated, and the residue of silver chloride weighed. Thus the process consisted in taking a known weight of silver chlorate, converting it into silver chloride, and determining the weight of the latter. The analysis conducted in this manner gave the following results, which, like the preceding, designate the weight in a vacuum calculated from the weights obtained in air. In the first experiment it appeared that 138.7890 grams of silver chlorate gave 103.9795 parts of silver chloride, and in the second experiment that 259.5287 grams of chlorate gave 194.44515 grams of silver chloride, and after fusion 194.4435 grams. The mean result of both experiments, converted into percentages, shows that 100 parts of silver chlorate contain 74.9205 of silver chloride and 25.0795 of oxygen. From this it is possible to calculate the combining weight of silver chloride, because in the decomposition of silver chlorate there are obtained three atoms of oxygen and one molecule of silver chloride: $\text{AgClO}_3 = \text{AgCl} + 3\text{O}$. Taking the weight of an atom of oxygen to be 16, we find from the mean result that the equivalent weight of silver chloride is equal to 143.395. Thus if $\text{O} = 16$, $\text{AgCl} = 143.395$, and as the preceding experiments show that silver chloride contains 32.8445 parts of chlorine per 100 parts of silver, the weight of the atom of silver^{25a} must be 107.94, and that of chlorine 35.45. The weight of the atom of sodium is determined from the fact that 21.3633 parts of sodium combine with 32.8445 parts of chlorine; consequently $\text{Na} = 23.05$. This conclusion, arrived at by the analysis of silver chlorate, was verified by means of the analysis of potassium chlorate by decomposing it by heat and determining the weight of the potassium chloride formed, and also by effecting the same decomposition by igniting the chlorate in a stream of hydrochloric acid. The combining weight of potassium

sary during drying to prevent the access of any organic matter; this is done by filtering the air through cotton-wool, and passing it over a layer of red-hot copper oxide.

^{25a} The results given by Stas's determinations have recently been recalculated and certain corrections have been introduced. We give the average results of van der Plaats's, Thomsen's, and Clark's calculations in the context, as well as in the table given in the Preface, neglecting the doubtful thousandths.

chloride was thus determined, and another series of determinations confirmed the relation between chlorine, potassium, and silver, in the same manner as the relation between sodium, chlorine, and silver was determined above. Consequently, the combining weights of sodium, chlorine, and potassium could be deduced by combining these data with the analysis of silver chlorate and the synthesis of silver chloride. The agreement between the results showed that the determinations made by the last method were perfectly correct, and did not depend in any considerable degree on the methods which were employed in the preceding determinations, as the combining weights of chlorine and silver obtained were the same as before. There was naturally a difference, but so small a one that it undoubtedly depended on the errors incidental to every process of weighing and experiment. The atomic weight of silver was also determined by Stas by means of the synthesis of silver sulphide and the analysis of silver sulphate. The combining weight obtained by this method was 107.920. The synthesis of silver iodide and the analysis of silver iodate gave the figure 107.928. The synthesis of silver bromide with the analysis of silver bromate gave the figure 107.921. The synthesis of silver chloride and the analysis of silver chlorate gave a mean result of 107.937. Hence there is no doubt that the combining weight of silver is at least as much as 107.9—greater than 107.90 and less than 107.95, and probably equal to the mean, 107.92. Stas determined in this manner the combining weights of many other elements, such as lithium, potassium, sodium, bromine, chlorine, iodine, and also nitrogen, for the determination of the amount of silver nitrate obtained from a given amount of silver gives directly the combining weight of nitrogen.

The exhaustive investigations conducted by Stas on the atomic weights of the above-named elements have great significance in the solution of the problem as to whether the atomic weights of the elements can be expressed in whole numbers if the unit taken be the atomic weight of hydrogen. Prout, at the beginning of the last century, stated that this was the case, and held that the atomic weights of the elements are multiples of the atomic weight of hydrogen. The subsequent determinations of Berzelius, Penny, Marchand, Marignac, Dumas, and more especially of Stas, proved this conclusion to be untenable, since a whole series of elements proved to have fractional atomic weights—for example, chlorine, about 35.5. On account of this, Marignac and Dumas stated that the atomic weights of the elements are expressed in relation to hydrogen, either by whole numbers or by numbers with simple fractions of the magnitudes $\frac{1}{2}$ and $\frac{1}{4}$. But Stas's researches refute this supposition also. Even between the com-

bining weight of hydrogen and oxygen, there is not, so far as is yet known, that simple relation which is required by **Prout's hypothesis**,²⁷

²⁷ This hypothesis, for the establishment or refutation of which so many researches have been made, is exceedingly important, and fully deserves the attention which has been given to it. Indeed, if it appeared that the atomic weights of all the elements could be expressed in whole numbers with reference to hydrogen, or if at least they proved to be commensurable with one another, then it could be affirmed with confidence that the elements, with all their diversity, were formed of one material (qualitative) condensed or grouped in various manners into the stable, and, under known conditions, undecomposable groups which we call the atoms of the elements. At first it was supposed that all the elements were nothing else than condensed hydrogen; but when it appeared that the atomic weights of the elements could not be expressed in whole numbers in relation to hydrogen, it was still possible to imagine the existence of a certain material from which both hydrogen and all the other elements were formed. If it should transpire that four atoms of this material form an atom of hydrogen, then the atom of chlorine would present itself as consisting of 142 atoms of this substance, the weight of whose atom would be equal to 0.25. But in this case the atoms of all the elements should be expressed in whole numbers with respect to the weight of the atom of this original material. Let us suppose that the atomic weight of this material is equal to unity, then all the atomic weights should be expressible in whole numbers relatively to this unit. Thus the atom of one element, let us suppose, would weigh m , and that of another n ; but, as both m and n must be whole numbers, it follows that the atomic weights of all the elements would be commensurable. But it is sufficient to glance over the results obtained by Stas, and to be assured of their accuracy, especially for silver, in order to entirely destroy, or at least strongly undermine, this attractive hypothesis. We must therefore *refuse our assent* to the doctrine of the building up from a single substance of the elements known to us. This hypothesis is not supported either by any known transformation (for one element has never been converted into another element), or by the commensurability of the atomic weights of the elements. Although the hypothesis of the formation of all the elements from a single substance (for which Crookes has suggested the name 'protyle') is most attractive in its comprehensiveness, it can neither be denied nor accepted for want of sufficient data. Marignac endeavoured, however, to overcome Stas's conclusions as to the incommensurability of the atomic weights by supposing that in his, as in the determinations of all other observers, there were unperceived errors which were quite independent of the mode of observation; for example, silver nitrate might be supposed to be an unstable substance which changes, under the heatings, evaporations, and other processes to which it is subjected in the reactions for the determination of the combining weight of silver. It might be supposed, for instance, that silver nitrate contains some impurity which cannot be removed by any means; it might also be supposed that a portion of the elements of the nitric acid are disengaged in the evaporation of the solution of silver nitrate (owing to the decomposing action of water), and in its fusion, and that we have to deal not with normal silver nitrate, but with a slightly basic salt, or perhaps an excess of nitric acid which cannot be removed from the salt. In this case the observed combining weight will not refer to an actually definite chemical compound, but to some mixture for which there do not exist any perfectly exact combining relations. Marignac upholds this proposition by the fact that the conclusions of Stas and other observers respecting the combining weights determined with the greatest exactitude very nearly agree with the proposition of the commensurability of the atomic weights; for example, the combining weight of silver was shown to be equal to 107.92, so that it only differs by 0.08 from the whole number 108, which is sometimes accepted for silver. The combining weight of iodine proved to be equal to 126.85—that is, it differs from 127 by 0.15. The combining weights of sodium, nitrogen, bromine, chlorine, and lithium are still nearer to the whole or round numbers, which are sometimes accepted. But Marignac's proposition will hardly bear criticism. Indeed, if we express the combining weights of the elements determined by Stas in relation to hydrogen, the approximation of these weights to whole numbers

i.e., taking $O = 16$, the atomic weight of hydrogen is equal not to 1 but to a greater number not less than 1.007 and not more than 1.009 or, say, 1.008. Such a conclusion arrived at by direct experiment cannot but be regarded as having greater weight than Prout's supposition (hypothesis) that the atomic weights of the elements are in multiple

disappears, because one part of hydrogen does not in reality combine with 16 parts of oxygen, but with 15.87 parts, and therefore we shall obtain, taking $H = 1$, not the above-cited figures, but for silver 107.12, for bromine 79.36—magnitudes which are still further removed from whole numbers. Besides which, if Marignac's proposition were true, the combining weight of silver determined by one method—e.g., by the analysis of silver chlorate combined with the synthesis of silver chloride—would not agree well with the combining weight determined by another method—e.g., by means of the analysis of silver iodate and the synthesis of silver iodide. If in one case a basic salt could be obtained, in the other case an acid salt might be obtained. Then the analysis of the acid salt would give different results from that of the basic salt. Thus Marignac's arguments cannot serve as a support for the vindication of Prout's hypothesis.

In conclusion, I think it will not be out of place to cite the following passage from a paper I read before the Chemical Society of London in 1889 (Appendix II.), referring to the hypothesis of the complexity of the elements recognised in chemistry, owing to the fact that many have endeavoured to apply the periodic law to the justification of this idea, dating from a remote antiquity, when it was found convenient to admit the existence of many gods but only one matter.

'When we try to explain the origin of the idea of a unique primary matter, we easily trace that, in the absence of deductions from experiment, it derives its origin from the scientifically philosophical attempt at discovering some kind of unity in the immense diversity of individualities which we see around. In classical times such a tendency could only be satisfied by conceptions about the immaterial world. As to the material world, our ancestors were compelled to resort to some hypothesis, and they adopted the idea of unity in the formative material, because they were not able to evolve the conception of any other possible unity in order to connect the multifarious relations of matter. Responding to the same legitimate scientific tendency, natural science has discovered throughout the universe a unity of plan, a unity of forces, and a unity of matter; and the convincing conclusions of modern science compel everyone to admit these kinds of unity. But while we admit unity in many things, we none the less must also explain the individuality and the apparent diversity which we cannot fail to trace everywhere. It was said of old "Give us a fulcrum and it will become easy to displace the earth." So also we must say, "Give us something that is individualised, and the apparent diversity will be easily understood." Otherwise, how could unity result in a multitude?

'After a long and painstaking research, natural science has discovered the individualities of the chemical elements, and is therefore now capable, not only of analysing, but also of synthesising; it can understand and grasp generality and unity, as well as the individualised and multifarious. The general and universal, like time and space, like force and motion, vary uniformly. The uniform admit of interpolations, revealing every intermediate phase; but the multitudinous, the individualised—such as ourselves, or the chemical elements, or the members of a peculiar periodic function of the elements, or Dalton's multiple proportions—is characterised in another way. We see in it, side by side with a general connecting principle—leaps, breaks of continuity, points which escape from the analysis of the infinitely small—an absence of complete intermediate links. Chemistry has found an answer to the question as to the causes of multitudes, and while retaining the conception of many elements, all submitted to the discipline of a general law, it offers an escape from the Indian Nirvana—the absorption in the universal—replacing it by the individualised. However, the place for individuality is so limited by the all-grasping, all-powerful universal that it is merely a point of support for the understanding of multitude in unity.'

proportion to each other, which would give reason for surmising (but not asserting) a complexity of nature in the elements, and their common origin from a single primary material, and for expecting their mutual conversion into each other. All such ideas and hopes must now, thanks more especially to Stas, be placed in a region void of any experimental support whatever, and therefore not subject to the discipline of the positive data of science.

Among the platinum metals, ruthenium, rhodium, and palladium, by their atomic weights and properties, approach silver, just as iron and its analogues (cobalt and nickel) approach copper in all respects. **Gold** stands in exactly the same position in relation to the heavy platinum metals, osmium, iridium, and platinum, as copper and silver do to the two preceding series. The atomic weight of gold is nearly equal to their atomic weights:²³ it is dense like these metals. It also gives various degrees of oxidation, which are feeble, in both a basic and an acid sense. Whilst near to osmium, iridium, and platinum, gold at the same time is able, like copper and silver, to form compounds which answer to the type RX —that is, oxides of the composition R_2O . Cuprous chloride, $CuCl$, silver chloride, $AgCl$, and aurous chloride, $AuCl$, are substances which are very much alike in their physical and chemical properties.^{23a} They are insoluble in water,

²³ It might be expected from the periodic law and analogies with the series iron, cobalt, nickel, copper, zinc, that the atomic weights of the elements of the series osmium, iridium, platinum, gold, mercury, would rise in this order, and at the time of the establishment of the periodic law (1869), the determinations of Berzelius, Rose, and others gave the following values for the atomic weights: $Os=200$, $Ir=197$, $Pt=198$, $Au=196$, $Hg=200$. The fulfilment of the expectations of the periodic law was given in the first place by the fresh determinations (Seubert, Dittmar, and Arthur) of the atomic weight of platinum, which proved to be nearly 195, if $O=16$ (as Marignac, Brauner, and others propose); in the second place, by the fact that Seubert proved that the atomic weight of osmium is really less than that of platinum, and approximately $Os=191$; and, in the third place, by the fact that after the researches of Kriess, Thorpe, and Laurie there was no doubt that the atomic weight of gold is greater than that of platinum—namely, nearly 197.

^{23a} In Chap. XXII., note 40, we gave the thermal data for certain of the compounds of copper of the type CuX_2 ; we shall now cite certain data for the cuprous compounds of the type CuX , which present an analogy to the corresponding compounds AgX and AuX , some of which were investigated by Thomsen in his classical work, *Thermochemische Untersuchungen* (vol. iii., 1883). The data are given in the same manner as in the above-mentioned note:

R =	Cu	Ag	Au
R + Cl	+ 33	+ 29	+ 6
R + Br	+ 25	+ 23	0
R + I	+ 16	+ 14	- 6
$R_2 + O$	+ 41	+ 6	- ?

Thus, we see in the first place that gold, which possesses a much smaller affinity than Ag , evolves far less heat than an equivalent amount of copper, giving the corresponding

but dissolve in hydrochloric acid and ammonia, in potassium cyanide, sodium thiosulphate, &c. Just as copper forms a link between the iron metals and zinc, and as silver unites the light platinum metals with cadmium, so also gold presents a transition from the heavy platinum metals to mercury. Copper gives saline compounds of the types CuX and CuX_2 , silver of the type AgX , whilst gold, besides compounds of the type AuX , very easily and most frequently forms those of the type AuCl_3 . The compounds of this type frequently pass into those of the lower type, just as PtX_4 passes into PtX_2 , and the same is observable in the elements which, in their atomic weights, follow gold. Mercury gives HgX_2 and HgX , thallium TlX_3 and TlX , and lead PbX_4 and PbX_2 . On the other hand, gold in a qualitative respect differs from silver and copper in the **extreme ease** with which all its compounds are **reduced to metal** by many means. This is accomplished not only by many reducing agents, but also by the action of heat. Thus, its chlorides and oxides lose their chlorine and oxygen when heated, and, if the temperature is sufficiently high, these elements are entirely expelled and metallic gold alone remains. Its compounds, therefore, act as oxidising agents.²⁹

In nature gold occurs in the primary and chiefly in quartzose rocks, and especially in quartz veins, as in the Urals (at Berezoffsk), in Australia, and in California. The native gold is extracted from these rocks by subjecting them to a mechanical treatment consisting of

compound, and in the second place that the combination of copper with one atom of oxygen disengages more heat than its combination with a halogen, whilst with silver the reverse is the case. This is connected with the fact that Cu_2O is more stable under the action of heat than Ag_2O .

²⁹ Heavy atoms and molecules, although they may present many points of analogy, are more easily isolated; thus $\text{C}_{16}\text{H}_{32}$, although, like C_2H_4 , it combines with Br_2 , and has a similar composition, yet reacts with much greater difficulty than C_2H_4 , and in this it resembles gold. The heavy atoms and molecules are, as it were, inert, and already saturated by themselves. Gold in its higher degree of oxidation, Au_2O_3 , presents feeble basic properties and weakly developed acid properties, so that this oxide of gold, Au_2O_3 , may be referred to the class of feeble acid oxides, like platiuc oxide. This is not the case with the highest known oxides of copper and silver. But in the lower grade of oxidation, aurous oxide, Au_2O , gold, like silver and copper, presents basic properties, although they are not very pronounced. In this respect it stands very close in its properties, although not in its types of combination (AuX and AuX_3), to platinum (PtX_2 and PtX_4) and its analogues.

As yet the general chemical characteristics of gold and its compounds have not been fully investigated. This is partly due to the fact that very few researches have been undertaken on the compounds of this metal, owing to its inaccessibility for working in large quantities. As the atomic weight of gold is high ($\text{Au} = 197$), the preparation of its compounds requires that it should be taken in large quantities, which forms an obstacle to its being fully studied. Hence the facts concerning the history of this metal are rarely distinguished by that exactitude with which many facts have been established concerning other elements more accessible, and long known in use.

crushing and washing.^{29a} Nature has already accomplished a similar disintegration of the hard rocky matter containing gold.³⁰ These

^{29a} Soustadt (1872) showed that sea water, besides silver, always contains gold. Munster (1892) showed that the water of the Norwegian fiords contains about 5 milligrams of gold per ton (or 5 milliardths), i.e., a quantity deserving practical attention, and I think it may be already said that, considering the immense amount of sea water, in time means will be discovered for profitably extracting gold from sea water by bringing it into contact with substances capable of depositing gold upon their surface. The first efforts might be made upon the extraction of salt from sea water, and as the total amount of sea water may be taken as about 2,000,000,000,000,000 tons, it follows that it contains about 10,000 million tons of gold. The yearly production of gold is about 700 tons for the whole world. It is supposed that gold is dissolved in sea water owing to the presence of iodides, which, under the action of animal organisms, yield free iodine. It is thought, as Professor Kouvaloff mentions, that iodine facilitates the solution of the gold, and the organic matter its precipitation. These facts and considerations explain to a certain extent the distribution of gold in veins or rock fissures, chiefly filled with quartz, because there is sufficient reason for supposing that these rocks once formed the ocean bottom. R. Dentry, and subsequently Wilkinson, showed that organic matter—for instance, cork—and pyrites are able to precipitate gold from its solutions in that metallic form and state in which it occurs in quartz veins, where (especially in the deeper parts of vein deposits) gold is frequently found on the surface of pyrites, chiefly arsenical pyrites. Kazantseff (in Ekaterinburg, 1891) even supposes, from the distribution of the gold in these pyrites, that it occurred in solution as a compound of sulphide of gold and sulphide of arsenic when it penetrated into the veins. It is from such considerations that the origin of vein and pyritic gold is, at the present time, attributed to the reaction of solutions of this metal, the remains of which are seen in the gold still present in sea water.

³⁰ However, in recent times, especially since about 1870, when chlorine (either as a solution of the gas or as bleaching powder) and bromine began to be applied to the extraction of finely divided gold from poor ores (previously roasted in order to drive off arsenic and sulphur and oxidise the iron), the extraction of gold from quartz and pyrites by the wet method, increases from year to year, and begins to equal the amount extracted from alluvial deposits. Since the nineties the *cyanide process* (Chap. XIII., note 12) has taken an important place among the wet methods for extracting gold from its ores. It consists in pouring a dilute solution of cyanide of potassium (about 500 parts of water and 1 to 4 parts of cyanide of potassium per 1,000 parts of ore, the amount of cyanide depending upon the richness of the ore) and a mixture of it with NaCN, over the crushed ore (which need not be roasted, whilst roasting is indispensable in the chlorination process, as otherwise the chlorine is used up in oxidising the sulphur, arsenic, &c.). The gold is dissolved very rapidly even from pyrites, where it generally occurs on the surface in such fine and adherent particles that it either cannot be mechanically washed away, or, more frequently, is carried away by the stream of water, and cannot be caught by mechanical means or by the mercury used for catching the gold in the sluices. Chlorination had already given the possibility of extracting the finest particles of gold; but the cyanide process enables such pyrites to be treated as could scarcely be worked by other means. The treatment of the crushed ore by the KCN is carried on in simple wooden vats (coated with paraffin or tar) with the greatest possible rapidity (in order that the KCN solution should not have time to change) by a method of systematic lixiviation, and is completed in 10 to 12 hours. The participation of the oxygen of the air is indispensable for the reaction (Chap. XIII., note 13a) for: $2\text{Au} + 4\text{KCN} + \text{O} + \text{H}_2\text{O} = 2(\text{KAuC}_2\text{N}_2) + 2\text{KHO}$. The resultant solution of gold, containing $\text{AuK}(\text{CN})_2$, is decomposed either with freshly made zinc filings (but when the gold settles on the Zn, the cyanide solution reacts upon the Zn with evolution of H_2 and formation of ZnH_2O_2) or by sodium amalgam prepared at the moment of reaction by the action of an electric current upon a solution of NaHO poured into a vessel partially immersed in mercury (the NaCN is

disintegrated rocks, washed by rain and other water, have formed gold-bearing deposits, which are known as **alluvial gold deposits**. Gold-bearing soil is sometimes met with on the surface and sometimes under the upper soil, but more frequently along the banks of dried-up water-courses and running streams. The sand of many rivers contains, however, a very small amount of gold, which it is not profitable to work; for example, that of the Alpine rivers contains 5 parts of gold in 10,000,000 parts of sand. The richest gold deposits are those of Siberia, especially in the southern parts of the government of Yeniseisk, the South Urals, Alaska, Mexico, California, South Africa, and Australia, and then come the comparatively poorer alluvial deposits of many countries (Hungary, the Alps, and Spain, in Europe). The extraction of the gold from alluvial deposits is based on the principle of levigation: the earth is washed, while constantly agitated, by a stream of water, which carries away the lighter portion of the earth, and leaves the coarser particles of the rock and heavier particles of the gold, together with certain substances which accompany it, in the washing apparatus. The extraction of this **washed gold** only necessitates mechanical appliances,³¹ and it is not therefore surprising that gold was known to

continually renewed by this means). The silver in the ore passes into solution, together with the gold, as in amalgamation.

³¹ But the particles of gold are sometimes so small that a large amount is lost during the washing. It is then profitable to have recourse to the extraction by chlorine and KCN (note 30). In speaking of the extraction of gold the following remarks may not be out of place: In California advantage is taken of water supplied from high altitudes in order to have a powerful head of water, with which the rocks are directly washed away, thus avoiding the greater portion of the mechanical labour required for the exploitation of these deposits. The last residues of gold are sometimes extracted from sand by washing them with mercury, which dissolves the gold. The sand mixed with water is caused to come into contact with mercury during the washing. The mercury is then distilled.

Many sulphurous ores, even pyrites, contain a small amount of gold. Compounds of gold with bismuth, BiAu_2 , tellurium, AuTe_2 (calverite), &c., have been found, although rarely.

Among the minerals which accompany gold, and from which the presence of gold may be expected, we may mention white quartz, titanite and magnetic iron ores, and also the following, which are of rarer occurrence: zircon, topaz, garnet, and the like. The concentrated gold washings first undergo a mechanical treatment, and the impure gold obtained is treated for pure gold by various methods. If the gold contains a considerable amount of foreign metals, especially lead and copper, it is sometimes cupelled, like silver, so that the oxidisable metals may be absorbed by the cupel in the form of oxides; but in every case the gold is obtained together with silver, because the latter metal also is not oxidised. Sometimes the gold is extracted by means of mercury, that is, by amalgamation (and the mercury subsequently driven off by distillation), or by smelting it with lead (which is afterwards removed by oxidation) and processes like those employed for the extraction of silver, because gold, like silver, does not oxidise, is dissolved by lead and mercury, and is non-volatile. If copper or any other metal contain gold and it be employed as an anode, pure copper will be deposited upon the cathode, while all the gold will remain at the anode as a slime. This method often amply repays the whole cost of the process, since it gives, besides the gold, a pure electrolytic copper.

savages and in the most remote periods of history. It sometimes occurs in crystals belonging to the regular system, but in the majority of cases in nuggets or grains of greater or less magnitude. It always contains silver (from very small quantities up to 30 per cent., when it is called 'electrum') and certain other metals, among which lead and rhodium are sometimes found. About 400 tons of gold are annually produced by the world, and about 40 tons by Russia.

The separation of the silver from gold is generally carried on with great precision, as the presence of silver in the gold does not increase its value for exchange, and it can be substituted by other less valuable metals, so that the extraction of the silver, as a precious metal, from its alloy with gold, is a profitable operation. This separation is conducted by different methods. Sometimes the argenti-ferous gold is melted in crucibles, together with a mixture of common salt and powdered bricks. The greater portion of the silver is thus converted into the chloride, which fuses and is absorbed by the slags, from which it may be extracted by the usual methods. The silver is also extracted from gold by treating it with boiling sulphuric acid, which does not act on the gold but dissolves the silver. But if the alloy does not contain a large proportion of silver it cannot be extracted by this method, or at all events the separation will be imperfect, and therefore a fresh amount of silver is added (by fusion) to the gold, in such quantity that the alloy contains twice as much silver as gold (quartation). The silver which is added is preferably such as contains gold, which is very frequently the case. The alloy thus formed is poured in a thin stream into water, by which means it is obtained in a granulated form; it is then boiled with strong sulphuric acid, three parts of acid being used to one part of alloy. The sulphuric acid extracts all the silver without acting on the gold. It is best, however, to pour off the first portion of the acid, which has dissolved the silver, and then treat the residue of still imperfectly pure gold with a fresh quantity of sulphuric acid. The gold is thus obtained in the form of powder, which is washed with water until it is quite free from silver. The silver is precipitated from the solution by means of copper, so that cupric sulphate and metallic silver are obtained. This process is carried out in many countries, as in Russia, at the Government mints.

Gold is generally used alloyed with copper; since pure gold, like pure silver, is very soft, and therefore soon worn away. In assaying or determining the amount of pure gold in such an alloy it is usual to add silver to the gold in order to make up an alloy containing three parts of silver to one of gold (this is known as

quartation because the alloy contains $\frac{1}{4}$ of gold), the resultant alloy being treated with nitric acid. If the silver is not in excess over the gold, it is not all dissolved by the nitric acid, and this is the reason for the quartation. The amount of pure gold (assay) is determined by weighing the gold which remains after this treatment. Russian, French, and other gold coin, and also many gold articles, are composed of an alloy containing 90 per cent. of gold. English gold coin contains $\frac{11}{12}$ Au.

Pure gold may be obtained from gold alloys by dissolving in aqua regia, and then adding ferrous sulphate to the solution or heating it with a solution of oxalic acid. These deoxidising agents reduce the gold, but not the other metals. The chlorine combined with the gold then acts like free chlorine. The gold, thus reduced, is precipitated as an exceedingly fine brown powder.^{31a} It is then washed with water, and fused with nitre or borax. Pure gold reflects a yellow light, and in the form of very thin sheets (gold-leaf), into which it can be hammered and rolled,^{31b} it transmits a bluish-green light. The specific gravity of gold is about 19.5, that of gold coin being about 17.1. It fuses at 1090°—at a higher temperature than silver—and can be drawn into exceedingly fine wires or hammered into thin sheets. With its softness and ductility, gold is distinguished for its tenacity, and a gold wire two millimetres thick breaks only under a load of 68 kilograms. Gold vaporises even at a furnace heat, and imparts a greenish colour to a flame passing over it in a furnace. Gold alloys with copper almost without changing its volume.³² In its chemical aspect, gold presents,

^{31a} Schottländer (1893) obtained gold in a soluble colloidal form (the solution is violet) by the action of a mixture of solutions of cerium acetate and NaHO upon a solution of AuCl₃. The gold separates out from such a solution in exactly the same manner as Ag does from the solution of colloidal silver mentioned above. There always remains a certain amount of a higher oxide of cerium, CeO₂, in the solution, i.e., the gold is reduced by converting the cerium into a higher grade of oxidation. Besides which, Kriess and Hofmann showed that sulphide of gold, precipitated by the action of H₂S upon a solution of AuKCy₂ mixed with HCl, easily passes into a colloidal solution after being properly washed (like As₂S₃, CuS, &c., Chap. I., note 57).

^{31b} Gold-leaf is used for gilding wood (leather, cardboard, and similar material, upon which it is glued by means of varnish, &c.), and is about 0.003 millimetre thick. It is obtained from thin sheets (weighing at first about $\frac{1}{4}$ gm. to a square inch), rolled between gold rollers, by gradually hammering them (in packets of a number at once) between sheets of moist (but not wet) parchment, and then, after cutting them into four pieces, between a specially prepared membrane, which, when at the right degree of moisture, does not tear or stick together under the blows of the hammer.

³² The formation of the alloys Cu + Zn, Cu + Sn, Cu + Bi, Cu + Sb, Pb + Sb, Ag + Pb, Ag + Sn, Au + Zn, Au + Sn, &c., is accompanied by a contraction (and evolution of heat). The formation of the alloys Fe + Sb, Fe + Pb, Cu + Pb, Pb + Sn, Pb + Sb, Zn + Sb, Ag + Cu, Au + Cu, Au + Pb, takes place with a certain increase in volume. With regard to the alloys of gold, it may be mentioned that gold is only slightly dissolved by mercury (about 0.06 per cent., Dudley, 1890); the remaining portion forms a

as is already seen from its general characteristics given above, an example of the so-called noble metals, i.e., it is incapable of being oxidised at any temperature, and its oxide is decomposed when calcined. Only chlorine and bromine combine directly with it at the ordinary temperature, but many other metals and non-metals combine with it at a red heat—for example, sulphur, phosphorus, and arsenic. Mercury dissolves it with great ease. It dissolves in potassium cyanide in the presence of air; a mixture of sulphuric acid with nitric acid dissolves it with the aid of heat, although in small quantity. It is also soluble in aqua regia and in selenic acid. Sulphuric, hydrochloric, nitric, and hydrofluoric acids and the caustic alkalis do not act on gold, but a mixture of hydrochloric acid with such oxidising agents as evolve chlorine naturally dissolves it, like aqua regia.^{32a}

As regards the compounds of gold, they belong, as was said above, to the types AuX_3 and AuX . **Auric chloride** or **gold trichloride**, $AuCl_3$, which is formed when gold is dissolved in aqua regia, belongs to the former and higher of these types. The solution of this substance in water has a yellow colour, and it may be obtained pure by evaporating the solution in aqua regia to dryness, but not to the point of decomposition. If the evaporation proceeds to the point of crystallisation, compound of gold chloride and hydrochloric acid, $AuHCl_4$, is obtained, like the allied compounds of platinum; but it easily parts with the acid and leaves auric chloride, which fuses into a red-brown liquid, and then solidifies to a crystalline mass. If dry chlorine is passed over powdered gold it forms a mixture of aurous and auric chlorides, but the aurous chloride is also partly decomposed by water into

granular alloy, whose composition has not been definitely determined. Aluminium (and silicon) also have the capacity of forming alloys with gold. The presence of a small amount of aluminium lowers the melting-point of gold considerably (Roberts-Austen, 1892); thus, the addition of 4 per cent. of aluminium lowers it by $14\cdot28^\circ$, the addition of 10 per cent. of Al by $41\cdot7^\circ$; the latter alloy is white. The alloy $AuAl_2$ has a characteristic purple colour, and its melting-point is $32\cdot5^\circ$ above that of gold, which shows it to be a definite compound of the two metals. The melting-points of alloys richer in Al gradually fall to 660° —that is, below that of aluminium (665°).

Heycock and Neville (1892), in studying the triple alloys of Au, Cd, and Sn, observed a tendency in the gold to give compounds with Cd, and by sealing a mixture of Au and Cd in a tube, from which the air had been exhausted, and heating it, they obtained a grey crystalline brittle definite alloy, $AuCd$.

^{32a} Calderon (1892), at the request of some jewellers, investigated the cause of a peculiar alteration sometimes found on the surface of dead-gold articles, there appearing brownish and blackish spots, which widen and alter their form in course of time. He came to the conclusion that these spots are due to the appearance and development on the gold of peculiar micro-organisms (*Aspergillus niger* and *Micrococcus cimbarcus*), spores of which were found in abundance on the cotton-wool in which the gold articles had been kept.

gold and auric chloride. Auric chloride crystallises from its solutions as $\text{AuCl}_3 \cdot 2\text{H}_2\text{O}$, which easily loses water, and the dry chloride loses two-thirds of its chlorine at 185° , forming aurous chloride, whilst above 300° the latter chloride also loses its chlorine and leaves metallic gold. Auric chloride is the usual form in which gold occurs in solutions, and in which its salts are used in the arts and for chemical purposes. It is soluble in water, alcohol, and ether. Light has a reducing action on these solutions, and after a time metallic gold is deposited upon the sides of vessels containing the solution. Hydrogen when nascent, and even in a gaseous form, reduces gold from this solution to a metallic state. The reduction is more conveniently and usually effected by ferrous sulphate, and by the action of ferrous salts in general.³³

If a solution of potassium hydroxide is added to a solution of auric chloride, a precipitate is first formed, which re-dissolves in an excess of the alkali. On being evaporated under the receiver of an air-pump, this solution yields yellow crystals, which present the same composition as the double salts AuMCl_4 , with the substitution of the chlorine by oxygen—that is to say, **potassium aurate**, AuKO_2 , is formed, in crystals containing $3\text{H}_2\text{O}$. The solution has a distinctly alkaline reaction. **Auric oxide**, Au_2O_3 , separates when this alkaline solution is boiled with an excess of sulphuric acid. But it then still retains some alkali; however, it may be obtained in a pure state as a brown powder by dissolving in nitric acid and diluting with water. The brown powder decomposes below 250° into gold and oxygen. It is insoluble in water and in many acids, but it dissolves in alkalies, which shows the acid character of this oxide. A hydroxide, $\text{Au}(\text{OH})_3$, may be obtained as a brown powder by adding magnesium oxide to a solution of auric chlo-

³³ Stannous chloride as a reducing agent also acts on auric chloride, and gives a red precipitate known as **purple of Cassius**. This substance, which probably contains a mixture or compound of aurous oxide and tin oxide, is used as a red pigment for china and glass. Oxalic acid, on heating, reduces metallic gold from its salts, and this property may be taken advantage of for separating it from its solutions. The oxidation which then takes place in the presence of water may be expressed by the following equation: $2\text{AuCl}_3 + 3\text{C}_2\text{H}_2\text{O}_4 = 2\text{Au} + 6\text{HCl} + 6\text{CO}_2$. Nearly all organic substances have a reducing action on gold, and solutions of gold leave a violet stain on the skin.

Auric chloride, like platinum chloride, is distinguished for its clearly developed property of forming double salts. These double salts, as a rule, belong to the type AuMCl_4 . The compound of auric chloride with hydrochloric acid mentioned above evidently belongs to the same type. The compounds $2\text{KAuCl}_4 \cdot 5\text{H}_2\text{O}$; $\text{NaAuCl}_4 \cdot 2\text{H}_2\text{O}$; $\text{AuNH}_4\text{Cl}_4 \cdot \text{H}_2\text{O}$; $\text{Mg}(\text{AuCl}_4)_2 \cdot 2\text{H}_2\text{O}$, and the like are easily crystallised in well-formed crystals. Wells, Wheeler, and Penfield (1892) obtained RbAuCl_4 (reddish-yellow) and CsAuCl_4 (golden-yellow), and corresponding bromides (dark-coloured). AuBr_3 is extremely like the chloride. Auric cyanide is easily obtained in the form of a double salt of potassium, $\text{KAu}(\text{CN})_4$, by mixing saturated and hot solutions of potassium cyanide with auric chloride and then cooling.

ride and treating the resultant precipitate of magnesium aurate with nitric acid. This hydroxide loses water at 100° , and gives auric oxide.³⁴

The starting-point of the compounds of the type AuX ³⁵ is **gold monochloride** or **aurous chloride**, AuCl , which is formed, as mentioned above, by heating auric chloride at 185° . Aurous chloride forms a yellowish-white powder; this, when heated with water, is decomposed into metallic gold and auric chloride, which passes into solution: $3\text{AuCl} = \text{AuCl}_3 + 2\text{Au}$. This decomposition is accelerated by the action of light. Hence it is obvious that the compounds corresponding with aurous oxide are comparatively unstable. But this only refers to the simple compounds AuX ; some of the complex compounds, on the contrary, form the most stable compounds of gold. Such, for example, is the cyanide of gold and potassium, $\text{AuK}(\text{CN})_2$. It is formed, for instance, when finely divided gold dissolves in the presence of air in a solution of potassium cyanide: $4\text{KCN} + 2\text{Au} + \text{H}_2\text{O} + \text{O} = 2\text{KAu}(\text{CN})_2 + 2\text{KHO}$ (this reaction also proceeds with solid pieces of gold, although very slowly). The same compound is formed in solution when many compounds of gold are mixed with potassium cyanide, because if a higher compound of gold is taken, it is reduced

³⁴ If ammonia is added to a solution of auric chloride, it forms a yellow precipitate of the so-called fulminating gold, which contains gold, chlorine, hydrogen, nitrogen, and oxygen, but its formula is not known with certainty. It is probably a sort of ammonio-metallic compound, $\text{Au}_2\text{O}_3 \cdot 4\text{NH}_3$, or amide (like the mercury compound). This precipitate explodes at 140° , but when left in the presence of solutions containing ammonia it loses all its chlorine and becomes non-explosive. In this form the composition $\text{Au}_2\text{O}_3 \cdot 2\text{NH}_3 \cdot \text{H}_2\text{O}$ is ascribed to it, but this is uncertain. Auric sulphide, Au_2S_3 , is obtained by the action of hydrogen sulphide on a solution of auric chloride, and also directly by fusing sulphur with gold. It has an acid character, and therefore dissolves in sodium and ammonium sulphides.

³⁵ Many double salts of suboxide of gold belong to the type AuX —for instance, the cyanide corresponding to the type AuKX_2 , like PtK_2X_1 , with which we became acquainted in the last chapter. If auric chloride, AuCl_3 , is mixed with a solution of sodium thiosulphate, the gold passes into a colourless solution, which deposits colourless crystals of a double thiosulphate of gold and sodium, which are easily soluble in water but are precipitated by alcohol. The composition of this salt is $\text{Na}_3\text{Au}(\text{S}_2\text{O}_3)_2 \cdot 2\text{H}_2\text{O}$. The solution of this colourless and easily crystallisable salt has a sweet taste, and the gold is not separated from it by either ferrous sulphate or oxalic acid. This salt, which is known as **Fordos and Gelis' salt**, is used in medicine and photography. In general, aurous oxide exhibits a distinct inclination to the formation of similar double salts, as we saw also with PtX_2 —for example, it forms similar salts with sulphurous acid. Thus, if a solution of sodium sulphite is gradually added to a solution of oxide of gold in sodium hydroxide, the precipitate at first formed re-dissolves to a colourless solution, which contains the double salt $\text{Na}_3\text{Au}(\text{SO}_3)_2 = \text{AuNa}(\text{SO}_3\text{Na})_2$. The solution of this salt when mixed with barium chloride, forms first a precipitate of barium sulphite, and then a red barium double salt which corresponds with the above sodium salt.

The oxygen compound of the type AuX , **aurous oxide**, Au_2O , is obtained as a greenish-violet powder on mixing aurous chloride with potassium chloride in the cold. With hydrochloric acid this oxide gives gold and auric chloride, and when heated it easily splits up into oxygen and metallic gold.

by the potassium cyanide to aurous oxide, which dissolves in potassium cyanide and forms $\text{KAu}(\text{CN})_2$. This substance is soluble in water, and gives a colourless solution, which can be kept for a long time, and is employed in electro-gilding—that is, for coating other metallic objects with a layer of gold, which is deposited if the object is connected with the cathode, and the anode consists of a gold plate, and an electric current is passed between them.

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APPENDIX I

AN ATTEMPT TO APPLY TO CHEMISTRY ONE OF THE PRINCIPLES OF NEWTON'S NATURAL PHILOSOPHY

By PROFESSOR MENDELÉEFF

A LECTURE DELIVERED AT THE ROYAL INSTITUTION OF GREAT BRITAIN
ON FRIDAY, MAY 31, 1889

NATURE, inert to the eyes of the ancients, has been revealed to us as full of life and activity. The conviction that motion pervaded all things, which was first realised with respect to the stellar universe, has now extended to the unseen world of atoms. No sooner had the human understanding denied to the earth a fixed position and launched it along its path in space, than it was sought to fix immovably the sun and the stars. But astronomy has demonstrated that the sun moves with unswerving regularity through the star-set universe at the rate of about 50 kilometres per second. Among the so-called fixed stars are now discerned manifold changes and various orders of movement. Light, heat, electricity—like sound—have been proved to be modes of motion; to the realisation of this fact modern science is indebted for powers which have been used with such brilliant success, and which have been expounded so clearly at this lecture table by Faraday and by his successors. As, in the imagination of Dante, the invisible air became peopled with spiritual beings, so before the eyes of earnest investigators, and especially before those of Clerk Maxwell, the invisible mass of gases became peopled with particles: their rapid movements, their collisions, and impacts became so manifest that it seemed almost possible to count the impacts and determine many of the peculiarities or laws of their collisions. The fact of the existence of these invisible motions may at once be made apparent by demonstrating the difference in the rate of diffusion through porous bodies of the light and rapidly moving atoms of hydrogen and the heavier and more sluggish particles of air. Within the masses of liquid and of solid bodies we have been forced to acknowledge the existence of persistent though limited motion of their ultimate particles, for otherwise it would be impossible to explain, for example, the celebrated experiments of Graham on diffusion through liquid and colloidal substances. If there were, in our times, no belief in the

molecular motion in solid bodies, could the famous Spring have hoped to attain any result by mixing carefully dried powders of potash, saltpetre, and sodium acetate, in order to produce, by pressure, a chemical reaction between these substances through the interchange of their metals, and have derived, for the conviction of the incredulous, a mixture of two hygroscopic though solid salts—sodium nitrate and potassium acetate?

In these invisible and apparently chaotic movements, reaching from the stars to the minutest atoms, there reigns, however, an harmonious order which is commonly mistaken for complete rest, but which is really a consequence of the conservation of that dynamic equilibrium which was first discerned by the genius of Newton, and which has been traced by his successors in the detailed analysis of the particular consequences of the great generalisation. namely, relative immovability in the midst of universal and active movement.

But the unseen world of chemical changes is closely analogous to the visible world of the heavenly bodies, since our atoms form distinct portions of an invisible world, as planets, satellites, and comets form distinct portions of the astronomer's universe; our atoms may therefore be compared to the solar systems, or to the systems of double or of single stars: for example, ammonia (NH_3) may be represented in the simplest manner by supposing the sun, nitrogen, surrounded by its planets of hydrogen; and common salt (NaCl) may be looked on as a double star formed of sodium and chlorine. Besides, now that the indestructibility of the elements has been acknowledged, chemical changes cannot otherwise be explained than as changes of motion, and the production by chemical reactions of galvanic currents, of light, of heat, of pressure, or of steam power, demonstrates visibly that the processes of chemical reaction are inevitably connected with enormous though unseen displacements, originating in the movements of atoms in molecules. Astronomers and natural philosophers, in studying the visible motions of the heavenly bodies and of matter on the earth, have understood and have estimated the value of this store of energy. But the chemist has had to pursue a contrary course. Observing in the physical and mechanical phenomena which accompany chemical reactions the quantity of energy manifested by the atoms and molecules, he is constrained to acknowledge that within the molecules there exist atoms in motion, endowed with an energy which, like matter itself, is neither being created nor capable of being destroyed. Therefore, in chemistry, we must seek dynamic equilibrium not only between the molecules, but also in their midst among their component atoms. Many conditions of such equilibrium have been determined, but much remains to be done, and it is not uncommon, even in these days, to find that some chemists forget that there is the possibility of motion in the interior of molecules, and therefore represent them as being in a condition of deathlike inactivity.

Chemical combinations take place with so much ease and rapidity, possess so many special characteristics, and are so numerous, that their simplicity and order were for a long time hidden from investigators. Sympathy, relationship, all the caprices or all the fancifulness of human intercourse, seemed to have found complete analogies in chemical combinations, but with this difference, that the characteristics of the material substances—such as silver, for example, or of any other body—remain unchanged in every sub-

division from the largest masses to the smallest particles, and consequently these characteristics must be properties of the particles. But the world of heavenly luminaries appeared equally fanciful at man's first acquaintance with it, so much so, that the astrologers imagined a connection between the individualities of men and the conjunctions of planets. Thanks to the genius of Lavoisier and of Dalton, man has been able, in the unseen world of chemical combinations, to recognise laws of the same simple order as those which Copernicus and Kepler proved to exist in the planetary universe. Man discovered, and continues every hour to discover, *what* remains unchanged in chemical evolution, and *how* changes take place in combinations of the unchangeable. He has learned to predict, not only what possible combinations may take place, but also the very existence of atoms of unknown elementary substances, and has besides succeeded in making innumerable practical applications of his knowledge to the great advantage of his race, and has accomplished this notwithstanding that notions of sympathy and affinity still preserve a strong vitality in science. At present we cannot apply Newton's principles to chemistry, because the soil is only now being prepared. The invisible world of chemical atoms is still waiting for the creator of chemical mechanics. For him our age is collecting a mass of materials, the inductions of well-digested facts, and many-sided inferences similar to those which existed for Astronomy and Mechanics in the days of Newton. It is well also to remember that Newton devoted much time to chemical experiments, and, while considering questions of celestial mechanics, persistently kept in view the mutual action of those infinitely small worlds which are concerned in chemical evolutions. For this reason, and also to maintain the unity of laws, it seems to me that we must, in the first instance, seek to harmonise the various phases of contemporary chemical theories with the immortal principles of the Newtonian natural philosophy, and so hasten the advent of true chemical mechanics. Let the above considerations serve as my justification for the attempt which I propose to make to act as a champion of the universality of the Newtonian principles, which I believe are competent to embrace every phenomenon in the universe, from the rotation of the fixed stars to the interchanges of chemical atoms.

In the first place I consider it indispensable to bear in mind that, up to quite recent times, only a one-sided affinity has been recognised in chemical reactions. Thus, for example, from the circumstance that red-hot iron decomposes water with the evolution of hydrogen, it was concluded that oxygen had a greater affinity for iron than for hydrogen. But hydrogen, in presence of red-hot iron scale, appropriates its oxygen and forms water, whence an exactly opposite conclusion may be formed.

During the last ten years a gradual, scarcely perceptible, but most important change has taken place in the views, and consequently in the researches, of chemists. They have sought everywhere, and have always found, systems of conservation or dynamic equilibrium substantially similar to those which natural philosophers have long since discovered in the visible world, and in virtue of which the position of the heavenly bodies in the universe is determined. There where one-sided affinities only were at first detected, not only secondary or lateral ones have been found, but even those

which are diametrically opposite ; yet among these, dynamical equilibrium establishes itself not by excluding one or other of the forces, but by regulating them all. So the chemist finds in the flame of the blast furnace, in the formation of every salt, and, with especial clearness, in double salts and in the crystallisation of solutions, not a fight ending in the victory of one side, as used to be supposed, but the conjunction of forces ; the peace of dynamic equilibrium resulting from the action of many forces and affinities. Carbonaceous matters, for example, burn at the expense of the oxygen of the air, yielding a quantity of heat, and forming products of combustion, in which it was thought that the affinities of the oxygen with the combustible elements were satisfied. But it appeared that the heat of combustion was competent to decompose these products, to dissociate the oxygen from the combustible elements, and therefore to explain combustion fully it is necessary to take into account the equilibrium between opposite reactions, between those which evolve and those which absorb heat.

In the same way, in the case of the solution of common salt in water, it is necessary to take into account, on the one hand, the formation of compound particles generated by the combination of salt with water, and, on the other, the disintegration or scattering of the new particles formed, as well as of these originally contained. At present we find two currents of thought, apparently antagonistic to each other, dominating the study of solutions : according to the one, solution seems a mere act of building up or association ; according to the other, it is only dissociation or disintegration. The truth lies, evidently, between these views ; it lies, as I have endeavoured to prove by my investigations into aqueous solutions, in the dynamic equilibrium of particles tending to combine and also to fall asunder. The large majority of chemical reactions which appeared to act victoriously along one line have been proved capable of acting as victoriously even along an exactly opposite line. Elements which utterly decline to combine directly may often be formed into comparatively stable compounds by indirect means, as, for example, in the case of chlorine and carbon ; and consequently the sympathies and antipathies which it was thought to transfer from human relations to those of atoms should be laid aside until the mechanism of chemical relations is explained. Let us remember, however, that chlorine, which does not form with carbon the chloride of carbon, is strongly absorbed, or, as it were, dissolved, by carbon, which leads us to suspect incipient chemical action even in an external and purely surface contact, and involuntarily gives rise to conceptions of that unity of the forces of nature which has been so energetically insisted on by Sir William Grove and formulated in his famous paradox. Grove noticed that platinum, when fused in the oxyhydrogen flame, during which operation water is formed, when allowed to drop into water decomposes the latter and produces the explosive oxyhydrogen mixture. The explanation of this paradox, as of many others which arose during the period of chemical renaissance, has led, in our time, to the promulgation by Henri Sainte-Claire Deville of the conception of dissociation and of equilibrium, and has recalled the teaching of Berthollet, which, notwithstanding its brilliant confirmation by Heinrich Rose and Dr. Gladstone, had not, up to that period, been included in received chemical views.

Chemical equilibrium in general, and dissociation in particular, are now being so fully worked out in detail, and applied in such various ways, that I do not allude to them to develop, but only use them as examples by which to indicate the correctness of a tendency to regard chemical combinations from points of view differing from those expressed by the term hitherto appropriated to define chemical forces, namely, 'affinity.' Chemical equilibria, dissociation, the speed of chemical reactions, thermochemistry, spectroscopy, and, more than all, the determination of the influence of masses and the search for a connection between the properties and weights of atoms and molecules—in one word, the vast mass of the most important chemical researches of the present day—clearly indicate the near approach of the time when chemical doctrines will submit fully and completely to the doctrine which was first announced in the 'Principia' of Newton.

In order that the application of these principles may bear fruit it is evidently insufficient to assume that statical equilibrium reigns alone in chemical systems or chemical molecules: it is necessary to grasp the conditions of possible states of dynamical equilibria, and to apply to them kinetic principles. Numerous considerations compel us to renounce the idea of statical equilibrium in molecules, and the recent yet strongly supported appeals to dynamic principles constitute, in my opinion, the foundation of the modern teaching relating to atomicity, or the valency of the elements, which usually forms the basis of investigations into organic or carbon compounds.

This teaching has led to brilliant explanations of very many chemical relations and to cases of isomerism, or the difference in the properties of substances having the same composition. It has been so fruitful in its many applications and in the foreshadowing of remote consequences, especially respecting carbon compounds, that it is impossible to deny its claims to be ranked as a great achievement of chemical science. Its practical application to the synthesis of many substances of the most complicated composition entering into the structure of organised bodies, and to the creation of an unlimited number of carbon compounds, among which the colours derived from coal tar stand prominently forward, surpass the synthetical powers of Nature itself. Yet this teaching, as applied to the structure of carbon compounds, is not on the face of it directly applicable to the investigation of other elements, because in examining the first it is possible to assume that the atoms of carbon have always a definite and equal number of affinities, whilst in the combinations of other elements this is evidently inadmissible. Thus, for example, an atom of carbon yields only one compound with four atoms of hydrogen and one with four atoms of chlorine in the molecule, whilst the atoms of chlorine and hydrogen unite only in the proportions of one to one. Simplicity is here evident, and forms a point of departure from which it is easy to move forward with firm and secure tread. Other elements are of a different nature. Phosphorus unites with three and with five atoms of chlorine, and consequently the simplicity and sharpness of the application of structural conceptions are lost. Sulphur unites only with two atoms of hydrogen, but with oxygen it enters into higher orders of combination. The periodic relationship which exists among all the properties of the elements—such, for example, as their ability to enter into various combinations—and

their atomic weights, indicate that this variation in atomicity is subject to one perfectly exact and general law, and it is only carbon and its near analogues which constitute cases of permanently preserved atomicity. It is impossible to recognise, as constant and fundamental properties of atoms, powers which, in substance, have proved to be variable. But by abandoning the idea of permanence, and of the constant saturation of affinities—that is to say, by acknowledging the possibility of free affinities—many retain a comprehension of the atomicity of the elements ‘under given conditions’; and on this frail foundation they build up structures composed of chemical molecules, evidently only because the conception of manifold affinities gives, at once, a simple statical method of estimating the composition of the most complicated molecules.

I shall enter neither into details, nor into the various consequences following from these views, nor into the disputes which have sprung up respecting them (and relating especially to the number of isomerides possible on the assumption of free affinities), because the foundation or origin of theories of this nature suffers from the radical defect of being in opposition to dynamics. The molecule, as even Laurent expressed himself, is represented as an architectural structure, the style of which is determined by the fundamental arrangement of a few atoms, whilst the decorative details, which are capable of being varied by the same forces, are formed by the elements entering into the combination. It is on this account that the term ‘structural’ is so appropriate to the contemporary views of the above order, and that the ‘structuralists’ seek to justify the tetrahedral, plane, or prismatic disposition of the atoms of carbon in benzene. It is evident that the consideration relates to the statical position of atoms and molecules and not to their kinetic relations. The atoms of the structural type are like the lifeless pieces on a chess-board: they are endowed but with the voices of living beings, and are not those living beings themselves; acting, indeed, according to laws, yet each possessed of a store of energy which, in the present state of our knowledge, must be taken into account.

In the days of Haüy, crystals were considered in the same statical and structural light, but modern crystallographers, having become more thoroughly acquainted with their physical properties and their actual formation, have abandoned the earlier views, and have made their doctrines dependent on dynamics.

The immediate object of this lecture is to show that, starting with Newton’s third law of motion, it is possible to preserve to chemistry all the advantages arising from structural teaching, without being obliged to build up molecules in solid and motionless figures, or to ascribe to atoms definite limited valencies, directions of cohesion, or affinities. The wide extent of the subject obliges me to treat of only a small portion of it, namely, of *substitutions*, without specially considering combinations and decompositions, and even then limiting myself to the simplest examples, which, however, will throw open prospects embracing all the natural complexity of chemical relations. For this reason, if it should prove possible to form groups similar, for example, to H_4 or CH_6 as the remnants of molecules CH_4 or C_2H_2 , we shall not pause to consider them, because, as far as we know, they fall asunder into

two parts, $H_2 + H_2$ or $CH_4 + H_2$, as soon as they are even temporarily formed, and are incapable of separate existence, and therefore can take no part in the elementary act of substitution. With respect to the simplest molecules which we shall select—that is to say, those of which the parts have no separate existence, and therefore cannot appear in substitutions—we shall consider them according to the periodic law, arranging them in direct dependence on the atomic weight of the elements.

Thus, for example, the molecules of the simplest hydrogen compounds—

HF	H_2O	H_3N	H_4C
hydrofluoric acid	water	ammonia	methane

correspond with elements the atomic weights of which decrease consecutively

$$F = 19, \quad O = 16, \quad N = 14, \quad C = 12.$$

Neither the arithmetical order (1, 2, 3, 4 atoms of hydrogen) nor the total information we possess respecting the elements will permit us to interpolate into this typical series one more additional element; and therefore we have here, for hydrogen compounds, a natural base on which are built up those simple chemical combinations which we take as typical. But even they are competent to unite with each other, as we see, for instance, in the property which hydrofluoric acid has of forming a hydrate—that is, of combining with water; and a similar attribute of ammonia, resulting in the formation of a caustic alkali, $NH_3 \cdot H_2O$, or NH_4OH .

Having made these indispensable preliminary observations, I may now attack the problem itself and attempt to explain the so-called structure, or rather construction, of molecules—that is to say, their constitution and transformations—without having recourse to the teaching of ‘structuralists,’ but on Newton’s dynamical principles.

Of Newton’s three laws of motion, only the third can be applied directly to chemical molecules when regarded as systems of atoms among which it must be supposed that there exist common influences or forces, and resulting compounded relative motions. Chemical reactions of every kind are undoubtedly accomplished by changes in these internal movements, respecting the nature of which nothing is known at present, but the existence of which the mass of evidence collected in modern times forces us to acknowledge as forming part of the common motion of the universe, and as a fact further established by the circumstance that chemical reactions are always characterised by changes of volume or the relations between the atoms or the molecules. Newton’s third law, which is applicable to every system, declares that ‘action is also associated with reaction, and is equal to it.’ The brevity or conciseness of this axiom was, however, qualified by Newton in a more expanded statement, ‘the actions of bodies one upon another are always equal, and in opposite directions.’ This simple fact constitutes the point of departure for explaining dynamic equilibrium—that is to say, systems of conservancy. It is capable of satisfying even the dualists, and of explaining, without additional assumptions, the preservation of those chemical types which Dumas, Laurent, and Gerhardt created unit types, and those views of atomic combinations which the structuralists express by atomicity or the

valency of the elements, and, in connection with them, the various numbers of affinities. In reality, if a system of atoms or a molecule be given, then in it, according to the third law of Newton, each portion of atoms acts on the remaining portion in the same manner, and with the same force as the second set of atoms acts on the first. We infer directly from this consideration that both sets of atoms, forming a molecule, are not only equivalent with regard to themselves, as they must be according to Dalton's law, but also that they may, if united, replace each other. Let there be a molecule containing atoms A B C, it is clear that, according to Newton's law, the action of A on B C must be equal to the action of B C on A, and if the first action is directed on B C, then the second must be directed on A, and consequently then, where A can exist in dynamic equilibrium, B C may take its place and act in a like manner. In the same way the action of C is equal to the action of A B. In one word every two sets of atoms forming a molecule are equivalent to each other, and may take each other's place in other molecules, or, having the power of balancing each other, the atoms or their complements are endowed with the power of replacing each other. Let us call this consequence of an evident axiom 'the principle of substitution,' and let us apply it to those typical forms of hydrogen compounds which we have already discussed, and which, on account of their simplicity and regularity, have served as starting-points of chemical argument long before the appearance of the doctrine of structure.

In the type of hydrofluoric acid, HF, or in systems of double stars, are included a multitude of the simplest molecules. It will be sufficient for our purpose to recall a few: for example, the molecules of chlorine, Cl_2 , and of hydrogen, H_2 , and hydrochloric acid, HCl, which is familiar to all in aqueous solution as spirits of salt, and which has many points of resemblance with HF, HBr, HI. In these cases division into two parts can only be made in one way, and therefore the principle of substitution renders it probable that exchanges between the chlorine and the hydrogen can take place, if they are competent to unite with each other. There was a time when no chemist would even admit the idea of any such action; it was then thought that the power of combination indicated a polar difference of the molecules in combination, and this thought set aside all idea of the substitution of one component element by another.

Thanks to the observations and experiments of Dumas and Laurent fifty years ago, such fallacies were dispelled, and in this manner the principle of substitution was exhibited. Chlorine and bromine, acting on many hydrogen compounds, occupy immediately the place of their hydrogen, and the displaced hydrogen, with another atom of chlorine or bromine, forms hydrochloric acid or bromide of hydrogen. This takes place in all typical hydrogen compounds. Thus chlorine acts on this principle on gaseous hydrogen—reaction, under the influence of light, resulting in the formation of hydrochloric acid. Chlorine acting on the alkalis, constituted similarly to water, and even on water itself—only, however, under the influence of light and only partially because of the instability of HClO —forms by this principle bleaching salts, which are the same as the alkalis, but with their hydrogen replaced by chlorine. In ammonia and in methane, chlorine can also replace

the hydrogen. From ammonia is formed in this manner the so-called chloride of nitrogen, NCl_3 , which decomposes very readily with violent explosion on account of the evolved gases, and falls asunder as chlorine and nitrogen. Out of marsh gas, or methane, CH_4 , may be obtained consecutively, by this method, every possible substitution, of which chloroform, CHCl_3 , is the best known, and carbon tetrachloride, CCl_4 , the most instructive. But by virtue of the fact that chlorine and bromine act, in the manner shown, on the simplest typical hydrogen compounds, their action on the more complicated ones may be assumed to be the same. This can be easily demonstrated. The hydrogen of benzene, C_6H_6 , reacts feebly under the influence of light on liquid bromine, but Gustavson has shown that the addition of the smallest quantity of metallic aluminium causes energetic action and the evolution of large volumes of hydrogen bromide.

If we pass on to the second typical hydrogen compound—that is to say, water—its molecule, HOH , may be split up in two ways: either into an atom of hydrogen and a semi-molecule of hydrogen peroxide, HO , or into oxygen, O , and two atoms of hydrogen, H ; and therefore, according to the principle of substitution, it is evident that one atom of hydrogen can exchange with hydrogen oxide, HO , and two atoms of hydrogen, H , with one atom of oxygen, O .

Both these forms of substitution will constitute methods of oxidation—that is to say, of the entrance of oxygen into the compound—a reaction which is so common in nature as well as in the arts, taking place at the expense of the oxygen of the air or by the aid of various oxidising substances or bodies which part easily with their oxygen. There is no occasion to reckon up the unlimited number of cases of such oxidising reactions. It is sufficient to state that in the first of these oxygen is directly transferred, and the position, the chemical function, which hydrogen originally occupied, is, after the substitution, occupied by the hydroxyl. Thus ammonia, NH_3 , yields hydroxylamine, $\text{NH}_2(\text{OH})$, a substance which retains many of the properties of ammonia.

Methane and a number of other hydrocarbons yield, by substitution of the hydrogen by its oxide, methyl alcohol, $\text{CH}_3(\text{OH})$, and other alcohols. The substitution of one atom of oxygen for two atoms of hydrogen is equally common with hydrogen compounds. By this means alcoholic liquids containing ethyl alcohol, or spirits of wine, $\text{C}_2\text{H}_5(\text{OH})$, are oxidised until they become vinegar, or acetic acid, $\text{C}_2\text{H}_3\text{O}(\text{OH})$. In the same way caustic ammonia, or the combination of ammonia with water, $\text{NH}_3\text{H}_2\text{O}$, or $\text{NH}_4(\text{OH})$, which contains a great deal of hydrogen, by oxidation exchanges four atoms of hydrogen for two atoms of oxygen, and becomes converted into nitric acid, $\text{NO}_2(\text{OH})$. This process of conversion of ammonium salts into saltpetre goes on in the fields every summer, and with especial rapidity in tropical countries. The method by which this is accomplished, though complex, though involving the agency of all-permeating micro-organisms, is, in substance, the same as that by which alcohol is converted into acetic acid, or glycol, $\text{C}_2\text{H}_4(\text{OH})_2$, into oxalic acid, if we view the process of oxidation in the light of the Newtonian principles.

But while speaking of the application of the principle of substitution to

water, we need not multiply instances, but must turn our attention to two special circumstances which are closely connected with the very mechanism of substitutions.

In the first place, the replacement of two atoms of hydrogen by one atom of oxygen may take place in two ways, because the hydrogen molecule is composed of two atoms, and therefore, under the influence of oxygen, the molecule forming water may separate before the oxygen has time to take its place. It is for this reason that we find, during the conversion of alcohol into acetic acid, that there is an interval during which is formed aldehyde, C_2H_4O , which, as its very name implies, is 'alcohol dehydrogenatum,' or alcohol deprived of hydrogen. Hence aldehyde combined with hydrogen yields alcohol; and united to oxygen, acetic acid.

For the same reason there should be, and there actually are, intermediate products between ammonia and nitric acid, $NO_2(HO)$, containing either less hydrogen than ammonia, less oxygen than nitric acid, or less water than caustic ammonia. Accordingly we find, among the products of the deoxidation of nitric acid and the oxidation of ammonia, not only hydroxylamine, but also nitrous oxide, nitrous and nitric anhydrides. Thus, the production of nitrous acid results from the removal of two atoms of hydrogen from caustic ammonia and the substitution of the oxygen for the hydrogen, $NO(OH)$; or by the substitution, in ammonia, of three atoms of hydrogen by hydroxyl, $N(OH)_3$, and by the removal of water: $N(OH)_3 - H_2O = NO(OH)$. The peculiarities and properties of nitrous acid—as, for instance, its action on ammonia and its conversion, by oxidation, into nitric acid—are thus clearly revealed.

On the other hand, in speaking of the principle of substitution as applied to water, it is necessary to observe that hydrogen and hydroxyl, H and OH , are not only competent to unite, but also to form combinations with themselves, and thus become H_2 and H_2O_2 ; and such are hydrogen and the peroxide thereof. In general, if a molecule $A B$ exists, then molecules $A A$ and $B B$ can exist also. A direct reaction of this kind does not, however, take place in water, therefore undoubtedly, at the moment of formation, hydrogen reacts on hydrogen peroxide, as we can show at once by experiment; and further because hydrogen peroxide, H_2O_2 , exhibits a structure containing a molecule of hydrogen, H_2 , and one of oxygen, O_2 , either of which is capable of separate existence. The fact, however, may now be taken as thoroughly established, that, at the moment of combustion of hydrogen or of the hydrogen compounds, hydrogen peroxide is always formed, and not only so, but in all probability its formation invariably precedes the formation of water. This was to be expected as a consequence of the law of Avogadro and Gerhardt, which leads us to expect this sequence in the case of equal interactions of volumes of vapours and gases: and in hydrogen peroxide we actually have such equal volumes of the elementary gases.

The instability of hydrogen peroxide—that is to say, the ease with which it decomposes into water and oxygen, even at the mere contact of porous substances—accounts for the circumstance that it does not form a permanent product of combustion, and is not produced during the decomposition

of water. I may mention this additional consideration that, with respect to hydrogen peroxide, we may look for its effecting still further substitutions of hydrogen by means of which we may expect to obtain still more highly oxidised water compounds, such as H_2O_3 and H_2O_4 . These Schönbein and Bunsen have long been seeking, and Berthelot is investigating them at present. It is probable, however, that the reaction will stop at the last compound, because we find that, in a number of cases, the addition of four atoms of oxygen seems to form a limit. Thus, OsO_4 , KClO_4 , KMnO_4 , K_2SO_4 , Na_3PO_4 , and such like, represent the highest grades of oxidation.¹

As for the last forty years, from the times of Berzelius, Dumas, Liebig, Gerhardt, Williamson, Frankland, Kolbe, Kekulé, and Butleroff, most theoretical generalisations have centred round organic or carbon compounds, we will, for the sake of brevity, leave out the discussion of ammonia derivatives, notwithstanding their simplicity with respect to the doctrine of substitutions; we will dwell more especially on its application to carbon compounds, starting from methane, CH_4 , as the simplest of the hydrocarbons, containing in its molecule one atom of carbon. According to the principles enumerated we may derive from CH_4 every combination of the form CH_3X , CH_2X_2 , CHX_3 , and CX_4 , in which X is an element, or radicle, equivalent to hydrogen—that is to say, competent to take its place or to combine with it. Such are the chlorine substitutes already mentioned, such is wood-spirit, $\text{CH}_3(\text{OH})$, in which X is represented by the residue of water, and such are numerous other carbon derivatives. If we continue, with the aid of hydroxyl, further substitutions of the hydrogen of methane, we shall obtain successively $\text{CH}_2(\text{OH})_2$, $\text{CH}(\text{OH})_3$, and $\text{C}(\text{OH})_4$. But if, in proceeding thus, we bear in mind that $\text{CH}_2(\text{OH})_2$ contains two hydroxyls in the same form as hydrogen peroxide, H_2O_2 or $(\text{OH})_2$, contains them—and moreover not only in one molecule, but together, attached to one and the same atom of carbon—so here we must look for the same decomposition as that which we find in hydrogen peroxide, and accompanied also by the formation of water as an independently existing molecule; therefore $\text{CH}_2(\text{OH})_2$ should yield, as it actually does, immediately water and the oxide of methylene, CH_2O , which is methane with

¹ Because more than four atoms of hydrogen never unite with one atom of the elements, and because the hydrogen compounds (e.g., HCl , H_2S , H_3P , H_4Si) always form their highest oxides with four atoms of oxygen, and as the highest forms of oxides (OsO_4 , RuO_4) also contain four of oxygen, and eight groups of the periodic system, corresponding to the highest basic oxides R_2O , RO , R_2O_3 , RO_2 , R_2O_5 , RO_3 , R_2O_7 , and RO_4 , imply the above relationship, and because of the nearest analogues among the elements—such as Mg, Zn, Cd, and Hg; or Cr, Mo, W, and U; or Si, Ge, Sn, and Pt; or F, Cl, Br, and I, and so forth—not more than four are known, it seems to me that in these relationships there lies a deep interest and meaning with regard to chemical mechanics. But because, to my imagination, the idea of unity of design in Nature, either acting in complex celestial systems or among chemical molecules, is very attractive, especially because the atomic teaching at once acquires its true meaning, I will recall the following facts relating to the solar system. There are eight major planets, of which the four inner ones are not only separated from the four outer by asteroids, but differ from them in many respects, as, for example, in the smallness of their diameters and their greater density. Saturn with his ring has eight satellites, Jupiter and Uranus have each four. It is evident that in the solar systems also we meet with these higher numbers four and eight which appear in the combination of chemical molecules.

oxygen substituted for two atoms of hydrogen. Exactly in the same manner, out of $\text{CH}(\text{OH})_3$ are formed water and formic acid, $\text{CHO}(\text{OH})$, and out of $\text{C}(\text{OH})_4$ are produced water and carbonic acid, or directly carbonic anhydride, CO_2 , which will therefore be nothing else than methane with the double replacement of pairs of hydrogen by oxygen. As nothing leads to the supposition that the four atoms of hydrogen in methane differ one from the other, so it does not matter by what means we obtain any one of the combinations indicated—they will be identical; that is to say, there will be no case of actual isomerism, although there may easily be such cases of isomerism as have been distinguished by the term metamerism.

Formic acid, for example, has two atoms of hydrogen, one attached to the carbon left from the methane, and the other attached to the oxygen which has entered in the form of hydroxyl, and if one of them be replaced by some substance X it is evident that we shall obtain substances of the same composition, but of different construction, or of different orders of movement among the molecules, and therefore endowed with other properties and reactions. If X be methyl, CH_3 —that is to say, a group capable of replacing hydrogen because it is actually contained with hydrogen in methane itself—then by substituting this group for the original hydrogen we obtain acetic acid $\text{CCH}_3\text{O}(\text{OH})$, out of formic, and by substitution of the hydrogen in its oxide or hydroxyl we obtain methyl formate, $\text{CHO}(\text{OCH}_3)$. These substances differ so much from each other physically and chemically that at first sight it is hardly possible to admit that they contain the same atoms in identically the same proportions. Acetic acid, for example, boils at a higher temperature than water, and has a higher specific gravity than it, whilst its metameride, methyl formate, is lighter than water, and boils at 30° —that is to say, it evaporates very easily.

Let us now turn to carbon compounds containing two atoms of carbon to the molecule, as in acetic acid, and proceed to evolve them from methane by the principle of substitution. This principle declares at once that methane can only be split up in the four following ways:—

1. Into a group CH_3 equivalent with H. Let us call changes of this nature methylation.

2. Into a group CH_2 and H_2 . We will call this order of substitutions methylenation.

3. Into CH and H_3 , which commutations we will call acetylenation.

4. Into C and H_4 , which may be called carbonation.

It is evident that hydrocarbon compounds containing two atoms of carbon can only proceed from methane, CH_4 , which contains four atoms of hydrogen by the first three methods of substitution; carbonation would yield free carbon if it could take place directly, and if the molecule of free carbon—which is in reality very complex, that is to say, strongly polyatomic, as I have long since been proving by various means—could contain only C_2 like the molecules O_2 , H_2 , N_2 , and so on.

By methylation we should evidently obtain from marsh gas, ethane, $\text{CH}_3\text{CH}_3 = \text{C}_2\text{H}_6$.

By methylenation—that is, by substituting group CH_2 for H_2 —methane forms ethylene, $\text{CH}_2\text{CH}_2 = \text{C}_2\text{H}_4$.

By acetylenation—that is, by substituting three atoms of hydrogen, H_3 , in methane—by the remnant CH , we get acetylene, $CHCH = C_2H_2$.

If we have applied the principles of Newton correctly, there should not be any other hydrocarbons containing two atoms of carbon in the molecule. All these combinations have long been known, and in each of them we can produce not only those substitutions of which an example has been given in the case of methane, but also all the phases of other substitutions, as we shall find from a few more instances, by the aid of which I trust that I shall be able to show the great complexity of those derivatives which, on the principle of substitution, can be obtained from each hydrocarbon. Let us content ourselves with the case of ethane, CH_3CH_3 , and the substitution of the hydrogen by hydroxyl. The following are the possible changes:—

1. $CH_3CH_2(OH)$: this is nothing more than spirit of wine, or ethyl alcohol, $C_2H_5(OH)$ or C_2H_6O .

2. $CH_2(OH)CH_2(OH)$: this is the glycol of Würtz, which has shed so much light on the history of alcohol. Its isomeride may be $CH_3CH(OH)_2$, but as we have seen in the case of $OH(OH)_2$, it decomposes, giving off water, and forming aldehyde, CH_3CHO , a substance capable of yielding alcohol by uniting with hydrogen, and of yielding acetic acid by uniting with oxygen.

If glycol, $CH_2(OH)CH_2(OH)$, loses its water, it may be seen at once that it will not now yield aldehyde, CH_3CHO , but its isomeride, $\begin{array}{c} CH_2CH_2 \\ | \quad | \\ O \end{array}$, the oxide of ethylene. I have here indicated in a special manner the oxygen which has taken the place of two atoms of the hydrogen of ethane taken from different atoms of the carbon.

3. $CH_3C(OH)_3$ decomposed as $CH(OH)_3$, forming water and acetic acid, $CH_3CO(OH)$. It is evident that this acid is nothing else than formic acid, $CHO(OH)$, with its hydrogen replaced by methyl. Without examining further the vast number of possible derivatives, I will direct your attention to the circumstance that in dissolving acetic acid in water we obtain the maximum contraction with the greatest viscosity when to the molecule $CH_3CO(OH)$ is added a molecule of water, which is the proportion which would form the hydrate $CH_3C(OH)_3$. It is probable that the doubling of the molecule of acetic acid at temperatures approaching its boiling-point has some connection with this power of uniting with one molecule of water.

4. $CH_2(OH)C(OH)_3$ is evidently an alcoholic acid, and indeed this compound, after losing water, answers to glycolic acid, $CH_2(OH)CO(OH)$. Without investigating all the possible isomerides, we will note only that the hydrate $CH(OH)_2CH(OH)_2$ has the same composition as $CH_2(OH)C(OH)_3$, and although corresponding to glycol, and being a symmetrical substance, it becomes, on parting with its water, the aldehyde of oxalic acid, or the glyoxal of Debus, $CHOCHO$.

5. $CH(OH)_2C(OH)_3$, from the tendency of all the preceding, corresponds with glyoxylic acid, an aldehyde acid, $CHCCO(OH)$, because the group $CO(OH)$, or carboxyl, enters into the compositions of organic acids, and the group CHO defines the aldehyde function.

6. $C(OH)_3C(OH)_3$ through the loss of $2H_2O$ yields the bibasic oxalic acid

CO(OH)CO(OH) , which generally crystallises with $2\text{H}_2\text{O}$, following thus the normal type of hydration characteristic of ethane.²

Thus, by applying the principle of substitution, we can, in the simplest manner, derive not only every kind of hydrocarbon compound, such as the alcohols, the aldehyde-alcohols, aldehydes, alcohol-acids, and the acids, but also combinations analogous to hydrated crystals which usually are disregarded.

But even those unsaturated substances, of which ethylene, CH_2CH_2 , and acetylene, CHCH , are types, may be evolved with equal simplicity. With respect to the phenomena of isomerism, there are many possibilities among the hydrocarbon compounds containing two atoms of carbon, and without going into details it will be sufficient to indicate that the following formulæ, though not identical, will be isomeric substantially among themselves:— CH_3CHX_2 and $\text{CH}_2\text{XCH}_2\text{X}$, although both contain $\text{C}_2\text{H}_4\text{X}_2$; or CH_2CX_2 and CHXCHX , although both contain $\text{C}_2\text{H}_2\text{X}_2$, if by X we indicate chlorine or generally an element capable of replacing one atom of hydrogen, or capable of uniting with it. To isomerism of this kind belongs the case of aldehyde and the oxide of ethylene, to which we have already referred, because both have the composition $\text{C}_2\text{H}_4\text{O}$.

What I have said appears to me sufficient to show that the principle of substitution adequately explains the composition, the isomerism, and all the diversity of combination of the hydrocarbons, and I shall limit the further development of these views to preparing a complete list of every possible hydrocarbon compound containing three atoms of carbon in the molecule. There are eight in all, of which only five are known at present.³

Among those possible for C_3H_6 , there should be two isomerides, propylene and trimethylene, and they are both already known. For C_3H_4 , there should be three isomerides: allylene and allene are known, but the third has not yet been discovered; and for C_3H_2 , there should be two isomerides, though neither of them is known as yet. Their composition and structure are easily

² One more isomeride, $\text{CH}_2\text{CH(OH)}$, is possible—that is, secondary vinyl alcohol, which is related to ethylene, CH_2CH_2 , but derived by the principle of substitution from CH_4 . Other isomerides, of the composition $\text{C}_2\text{H}_4\text{O}$, such, for example, as $\text{CCH}_3\text{(OH)}$, are impossible, because it would correspond with the hydrocarbon $\text{CHCH}_3 = \text{C}_2\text{H}_4$, which is isomeric with ethylene, and it cannot be derived from methane. If such an isomeride existed it would be derived from CH_2 , but such products are, up to the present, unknown. In such cases the insufficiency of the points of departure of the statical structural teaching is shown. It first admits constant atomicity and then rejects it, the facts serving to establish either one or the other view; and therefore it seems to me that we must come to the conclusion that the structural method of reasoning, having done a service to science, has outlived the age, and must be regenerated, as in their time was the teaching of the electro-chemists, the radicalists, and the adherents of the doctrine of types. As we cannot now lean on the views above stated, it is time to abandon the structural theory. They will all be united in chemical mechanics, and the principle of substitution must be looked on only as a preparation for the coming epoch in chemistry, where such cases as the isomerism of fumaric and maleic acids, when explained dynamically, as proposed by Le Bel and van't Hoff, may yield points of departure.

³ Conceding variable atomicity, the structuralists must expect an incomparably larger number of isomerides, and they cannot now decline to acknowledge the change of atomicity, were it only for the examples HgCl and HgCl_2 , CO and CO_2 , PCl_3 and PCl_5 .

deduced from ethane, ethylene, and acetylene by methylation, by methylenation, by acetylation, and by carbonation.

1. $C_3H_8 = CH_3CH_2CH_3$ out of CH_3CH_3 by methylation. This hydrocarbon is named propane.

2. $C_3H_6 = CH_3CHCH_2$ out of CH_3CH_3 by methylenation. This substance is propylene.

3. $C_3H_6 = CH_2CH_2CH_2$ out of CH_3CH_3 by methylenation. This substance is trimethylene.

4. $C_3H_4 = CH_3CCH$ out of CH_3CH_3 by acetylenation or from $CHCH$ by methylation. This hydrocarbon is named allylene.

5. $C_3H_4 = \begin{smallmatrix} CHCH \\ CH_2 \end{smallmatrix}$ out of CH_3CH_3 by acetylenation, or from CH_2CH_2 by methylenation, because $\begin{smallmatrix} CH_2CH \\ CH \end{smallmatrix} = \begin{smallmatrix} CHCH \\ CH_2 \end{smallmatrix}$. This body is as yet unknown.

6. $C_3H_4 = CH_2CCH_2$ out of CH_2CH_2 by methylenation. This hydrocarbon is named allene, or iso-allylene.

7. $C_3H_2 = \begin{smallmatrix} CHCH \\ C \end{smallmatrix}$ out of CH_3CH_3 by symmetrical carbonation, or out of CH_2CH_2 by acetylation. This compound is unknown.

8. $C_3H_2 = \begin{smallmatrix} CC \\ CH_2 \end{smallmatrix}$ out of CH_3CH_3 by carbonation, or out of $CHCH$ by methylenation. This compound is unknown.

If we bear in mind that for each hydrocarbon serving as a type in the above tables there are a number of corresponding derivatives, and that every compound obtained may, by further methylation, methylenation, acetylation, and carbonation, produce new hydrocarbons, and these may be followed by a numerous suite of derivatives and an immense number of isomeric substances, it is possible to understand the limitless number of carbon compounds, although they all have the one substance, methane, for their origin. The number of substances is so enormous that it is no longer a question of enlarging the possibilities of discovery, but rather of finding some means of testing them analogous to the well-known two which for a long time have served as gauges for all carbon compounds.

I refer to the law of even numbers and to that of limits, the first enunciated by Gerhardt some forty years ago, with respect to hydrocarbons, namely, that their molecules always contain an even number of atoms of hydrogen. But by the method which I have used of deriving all the hydrocarbons from methane, CH_4 , this law may be deduced as a direct consequence of the principle of substitutions. Accordingly, in methylation, CH_3 takes the place of H, and therefore CH_2 is added. In methylenation the number of atoms of hydrogen remains unchanged, and at each acetylenation it is reduced by two, and in carbonation by four, atoms—that is to say, an even number of atoms of hydrogen is always added or removed. And because the fundamental hydrocarbon, methane, CH_4 , contains an even number of atoms of hydrogen, all its derivative hydrocarbons will also contain even numbers of hydrogen, and this constitutes the law of even numbers.

The principle of substitutions explains with equal simplicity the conception of the limiting compositions of hydrocarbons C_nH_{2n+2} , which I derived, in

1861,⁴ in an empirical manner from accumulated materials available at that time, and on the basis of the limits to combinations worked out by Dr. Frankland for other elements.

Of all the various substitutions the highest proportion of hydrogen is yielded by methylation, because in that operation alone does the quantity of hydrogen increase; hence, taking methane as a point of departure, if we imagine methylation effected $(n-1)$ times we obtain hydrocarbon compounds containing the highest quantities of hydrogen. It is evident that they will contain $\text{CH}_4 + (n-1)\text{CH}_2$, or $\text{C}_n\text{H}_{2n+2}$, because methylation leads to the addition of CH_2 to the compound.

It will thus be seen that by the principle of substitution—that is to say, by the third law of Newton—we are able to deduce, in the simplest manner, not only the individual composition, the isomerism, and relations of substances, but also the general laws which govern their most complex combinations without having recourse either to statical constructions, to the definition of atomicities, to the exclusion of free affinities, or to the recognition of those single, double, or treble bonds which are so indispensable to structuralists in the explanation of the composition and construction of hydrocarbon compounds. And yet, by the application of the dynamical principles of Newton, we can attain to that chief and fundamental object, the comprehension of isomerism in hydrocarbon compounds, and the forecasting of the existence of combinations as yet unknown, by which the edifice raised by structural teaching is strengthened and supported. Besides—and I count this for a circumstance of special importance—the process which I advocate will make no difference in those special cases which have been already so well worked out, such as, for example, the isomerism of the hydrocarbons and alcohols, even to the extent of not interfering with the nomenclature which has been adopted, and the structural system will retain all the glory of having worked up, in a thoroughly scientific manner, the store of information which Gerhardt had accumulated about the middle of the fifties, and the still higher glory of establishing the rational synthesis of organic substances. Nothing will be lost to the structural doctrine except its statical origin; and as soon as it will embrace the dynamic principles of Newton, and suffer itself to be guided by them, I believe that we shall attain for chemistry that unity of principle which is now wanting. Many an adept will be attracted to that brilliant and fascinating enterprise, the penetration into the unseen world of the kinetic relations of atoms, to the study of which the last twenty-five years have contributed so much labour and such high inventive faculties.

D'Alembert found in mechanics that if inertia be taken to represent force, dynamic equations may be applied to statical questions, which are thereby rendered more simple and more easily understood.

The structural doctrine in chemistry has unconsciously followed the same course, and therefore its terms are easily adopted; they may retain their present forms provided that a truly dynamical—that is to say, Newtonian—meaning be ascribed to them.

Before finishing my task and demonstrating the possibility of adapting

⁴ 'Essai d'une Théorie sur les Limites des Combinaisons organiques,' par D. Mendéléeff, 2/11 août 1861, *Bulletin de l'Académie i. d. Sc. de St-Petersbourg*, tom. v.

structural doctrines to the dynamics of Newton, I consider it indispensable to touch on one question which naturally arises, and which I have heard discussed more than once. If bromine, the atom of which is eighty times heavier than that of hydrogen, takes the place of hydrogen, it would seem that the whole system of dynamic equilibrium must be destroyed.

Without entering into the minute analysis of this question, I think it will be sufficient to examine it by the light of two well-known phenomena, one of which will be found in the department of chemistry and the other in that of celestial mechanics, and both will serve to demonstrate the existence of that unity in the plan of creation which is a consequence of the Newtonian doctrines. Experiments demonstrate that when a heavy element is substituted for a light one in a chemical compound—for example, for magnesium, in the oxide of that metal, an atom of mercury, which is $8\frac{1}{2}$ times heavier—the chief chemical characteristics or properties are generally, though not always, preserved.

The substitution of silver for hydrogen, than which it is 108 times heavier, does not affect all the properties of the substance, though it does some. Therefore chemical substitutions of this kind—the substitution of light for heavy atoms—need not necessarily entail changes in the original equilibrium; and this point is still further elucidated by the consideration that the periodic law indicates the degree of influence of an increment of weight in the atom as affecting the possible equilibria, and also what degree of increase in the weight of the atoms reproduces some, though not all, of the properties of the substance.

This tendency to repetition—these periods—may be likened to those annual or diurnal periods with which we are so familiar on the earth. Days and years follow each other, but, as they do so, many things change; and in like manner chemical evolutions, changes in the masses of the elements, permit of much remaining undisturbed, though many properties undergo alteration. The system is maintained according to the laws of conservation in nature, but the motions are altered in consequence of the change of parts.

Next, let us take an astronomical case—such, for example, as the earth and the moon—and let us imagine that the mass of the latter is constantly increasing. The question is, what will then occur? The path of the moon in space is a wave-line similar to that which geometers have named epicycloidal, or the locus of a point in a circle rolling round another circle. But in consequence of the influence of the moon it is evident that the path of the earth itself cannot be a geometric ellipse, even supposing the sun to be immovably fixed; it must be an epicycloidal curve, though not very far removed from the true ellipse—that is to say, it will be impressed with but faint undulations. It is only the common centre of gravity of the earth and the moon which describes a true ellipse round the sun. If the moon were to increase, the relative undulations of the earth's path would increase in amplitude, those of the moon would also change, and when the mass of the moon had increased to an equality with that of the earth, the path would consist of epicycloidal curves crossing each other and having opposite phases. But a similar relation exists between the sun and the earth, because the former is also moving in space. We may apply these views to the world of atoms, and

suppose that in their movements, when heavy ones take the place of those that are lighter, similar changes take place, provided that the system or the molecule is preserved throughout the change.

It seems probable that in the heavenly systems, during incalculable astronomical periods, changes have taken place and are still going on similar to those which pass rapidly before our eyes during the chemical reaction of molecules, and the progress of molecular mechanics may—we hope will—in course of time permit us to explain those changes in the stellar world which have more than once been noticed by astronomers, and which are now so carefully studied. A coming Newton will discover the laws of these changes. Those laws, when applied to chemistry, may exhibit peculiarities, but these will certainly be mere variations on the grand harmonious theme which reigns in nature. The discovery of the laws which produce this harmony in chemical evolution will only be possible, it seems to me, under the banner of Newtonian dynamics, which has so long waved over the domains of mechanics, astronomy, and physics. In calling chemists to take their stand under its peaceful and catholic shadow I imagine that I am aiding in establishing that scientific union which the managers of the Royal Institution wish to effect, who have shown their desire to do so by the flattering invitation which has given me—a Russian—the opportunity of laying before the countrymen of Newton an attempt to apply to chemistry one of his immortal principles.

APPENDIX II

THE PERIODIC LAW OF THE CHEMICAL ELEMENTS

By PROFESSOR MENDELÉEFF

FARADAY LECTURE DELIVERED BEFORE THE FELLOWS OF
THE CHEMICAL SOCIETY IN THE THEATRE OF THE ROYAL INSTITUTION
ON TUESDAY, JUNE 4, 1889

THE high honour bestowed by the Chemical Society in inviting me to pay a tribute to the world-famed name of Faraday by delivering this lecture has induced me to take for its subject the Periodic Law of the Elements, this being a generalisation in chemistry which has of late attracted much attention.

While science is pursuing a steady onward movement, it is convenient from time to time to cast a glance back on the route already traversed, and especially to consider the new conceptions which aim at discovering the general meaning of the stock of facts accumulated from day to day in our laboratories. Owing to the possession of laboratories, modern science now bears a new character, quite unknown, not only to antiquity, but even to the preceding century. Bacon's and Descartes' idea of submitting the mechanism of science simultaneously to experiment and reasoning has been fully realised in the case of chemistry, it having become not only possible but always customary to experiment. Under the all-penetrating control of experiment, a new theory, even if crude, is quickly strengthened, provided it be founded on a sufficient basis; the asperities are removed, it is amended by degrees, and soon loses the phantom light of a shadowy form or of one founded on mere prejudice; it is able to lead to logical conclusions, and to submit to experimental proof. Willingly or not, in science we all must submit not to what seems to us attractive from one point of view or from another, but to what represents an agreement between theory and experiment; in other words, to demonstrated generalisation and to the approved experiment. Is it long since many refused to accept the generalisations involved in the law of Avogadro and Ampère, so widely extended by Gerhardt? We still may hear the voices of its opponents; they enjoy perfect freedom, but vainly will their

voices rise so long as they do not use the language of demonstrated facts. The striking observations with the spectroscope which have permitted us to analyse the chemical constitution of distant worlds seemed, at first, applicable to the task of determining the nature of the atoms themselves; but the working out of the idea in the laboratory soon demonstrated that the characters of spectra are determined, not directly by the atoms, but by the molecules into which the atoms are packed; and so it became evident that more verified facts must be collected before it will be possible to formulate new generalisations capable of taking their place beside those ordinary ones based upon the conception of simple substances and atoms. But as the shade of the leaves and roots of living plants, together with the relics of a decayed vegetation, favour the growth of the seedling and serve to promote its luxuriant development, in like manner sound generalisations—together with the relics of those which have proved to be untenable—promote scientific productivity, and ensure the luxuriant growth of science under the influence of rays emanating from the centres of scientific energy. Such centres are scientific associations and societies. Before one of the oldest and most powerful of these I am about to take the liberty of passing in review the twenty years' life of a generalisation which is known under the name of the Periodic Law. It was in March 1869 that I ventured to lay before the then youthful Russian Chemical Society the ideas upon the same subject which I had expressed in my just written 'Principles of Chemistry.'

Without entering into details, I shall give the conclusions I then arrived at in the very words I used:—

'1. The elements, if arranged according to their atomic weights, exhibit an evident *periodicity* of properties.

'2. Elements which are similar as regards their chemical properties have atomic weights which are either of nearly the same value (e.g., platinum, iridium, osmium) or which increase regularly (e.g., potassium, rubidium, caesium).

'3. The arrangement of the elements, or of groups of elements, in the order of their atomic weights, corresponds to their so-called *valencies* as well as, to some extent, to their distinctive chemical properties—as is apparent, among other series, in that of lithium, beryllium, barium, carbon, nitrogen, oxygen, and iron.

'4. The elements which are the most widely diffused have *small* atomic weights.

'5. The *magnitude* of the atomic weight determines the character of the element, just as the magnitude of the molecule determines the character of a compound.

'6. We must expect the discovery of many yet *unknown* elements—for example, elements analogous to aluminium and silicon, whose atomic weight would be between 65 and 75.

'7. The atomic weight of an element may sometimes be amended by a knowledge of those of the contiguous elements. Thus, the atomic weight of tellurium must lie between 123 and 126, and cannot be 128.

'8. Certain characteristic properties of the elements can be foretold from their atomic weights.

'The aim of this communication will be fully attained if I succeed in drawing the attention of investigators to those relations which exist between the atomic weights of dissimilar elements, which, so far as I know, have hitherto been almost completely neglected. I believe that the solution of some of the most important problems of our science lies in researches of this kind.'

To-day, twenty years after the above conclusions were formulated, they may still be considered as expressing the essence of the now well-known periodic law.

Reverting to the epoch terminating with the sixties, it is proper to indicate three series of data without the knowledge of which the periodic law could not have been discovered, and which rendered its appearance natural and intelligible.

In the first place, it was at that time that the numerical value of atomic weights became definitely known. Ten years earlier such knowledge did not exist, as may be gathered from the fact that in 1860 chemists from all parts of the world met at Karlsruhe in order to come to some agreement, if not with respect to views relating to atoms, at any rate as regards their definite representation. Many of those present probably remember how vain were the hopes of coming to an understanding, and how much ground was gained at that Congress by the followers of the unitary theory so brilliantly represented by Cannizzaro. I vividly remember the impression produced by his speeches, which admitted of no compromise, and seemed to advocate truth itself, based on the conceptions of Avogadro, Gerhardt, and Regnault, which at that time were far from being generally recognised. And though no understanding could be arrived at, yet the objects of the meeting were attained, for the ideas of Cannizzaro proved, after a few years, to be the only ones which could stand criticism, and which represented an atom as 'the smallest portion of an element which enters into a molecule of its compound.' Only such real atomic weights—not conventional ones—could afford a basis for generalisation. It is sufficient, by way of example, to indicate the following cases in which the relation is seen at once and is perfectly clear:—

K = 39	Rb = 85	Cs = 133
Ca = 40	Sr = 87	Ba = 137

whereas with the equivalents then in use—

K = 39	Rb = 85	Cs = 133
Ca = 20	Sr = 43·5	Ba = 68·5

the consecutiveness of change in atomic weight, which with the true values is so evident, completely disappears.

Secondly, it had become evident during the period 1860–1870, and even during the preceding decade, that the relations between the atomic weights of analogous elements were governed by some general and simple laws. Cooke, Cremers, Gladstone, Gmelin, Lenssen, Pettenkofer, and especially Dumas, had already established many facts bearing on that view. Thus Dumas compared the following groups of analogous elements with organic radicles:—

Diff.	Diff.	Diff.	Diff.
	Mg = 12 } 8	P = 31 } 44	O = 8 } 8
Li = 7 } 16	Ca = 20 } 3 × 8	As = 75 } 44	S = 16 } 3 × 8
Na = 23 } 16	Sr = 44 } 3 × 8	Sb = 119 } 2 × 44	Se = 40 } 3 × 8
K = 39 } 16	Ba = 68 } 3 × 8	Bi = 207 } 2 × 44	Te = 64 } 3 × 8

and pointed out some really striking relationships, such as the following:—

$$F = 19.$$

$$Cl = 35.5 = 19 + 16.5.$$

$$Br = 80 = 19 + 2 \times 16.5 + 28.$$

$$I = 127 = 2 \times 19 + 2 \times 16.5 + 2 \times 28.$$

A. Strecker, in his work 'Theorien und Experimente zur Bestimmung der Atomgewichte der Elemente' (Braunschweig, 1859), after summarising the data relating to the subject, and pointing out the remarkable series of equivalents—

$$\begin{array}{ccccccccc} Cr = 26.2 & Mn = 27.6 & Fe = 28 & Ni = 29 & Co = 30 & Cu = 31.7 \\ & & Zn = 32.5 & & & \end{array}$$

remarks: 'It is hardly probable that all the above-mentioned relations between the atomic weights (or equivalents) of chemically analogous elements are merely accidental. We must, however, leave to the future the discovery of the *law* of the relations which appears in these figures.'¹

In such attempts at arrangement and in such views are to be recognised the real forerunners of the periodic law; the ground was prepared for it between 1860 and 1870, and that it was not expressed in a determinate form before the end of the decade may, I suppose, be ascribed to the fact that only analogous elements had been compared. The idea of seeking for a relation between the atomic weights of all the elements was foreign to the ideas then current, so that neither the *vis tellurique* of De Chancourtois, nor *law of octaves* of Newlands, could secure anybody's attention. And yet both De Chancourtois and Newlands, like Dumas and Strecker, more than Lenssen and Pettenkofer, had made an approach to the periodic law and had discovered its germs. The solution of the problem advanced but slowly, because the facts, but not the law, stood foremost in all attempts; and the law could not awaken a general interest so long as elements, having no apparent connection with each other, were included in the same octave; as, for example:—

1st octave of									
Newlands . .	H	F	Cl	Co & Ni	Br	Pd	I	Pt & Ir	
7th Ditto	O	S	Fe	Se	Rh & Ru	Te	Au	Os or Th	

Analogies of the above order seemed quite accidental, and the more so as the octave contained occasionally ten elements instead of eight, and when two

¹ 'Es ist wohl kaum anzunehmen, dass alle im vorhergehenden hervorgehobenen Beziehungen zwischen den Atomgewichten (oder Aequivalenten) in chemischen Verhältnissen einander ähnliche Elemente bloss zufällig sind. Die Auffindung der in diesen Zahlen *gesetzlichen* Beziehungen müssen wir jedoch der Zukunft überlassen.'

such elements as Ba and V, Co and Ni, or Rh and Ru, occupied one place in the octave.² Nevertheless, the fruit was ripening, and I now see clearly that Strecker, De Chancourtois, and Newlands stood foremost in the way towards the discovery of the periodic law, and that they merely wanted the boldness necessary to place the whole question at such a height that its reflection on the facts could be clearly seen.

A third circumstance which revealed the periodicity of chemical elements was the accumulation, by the end of the sixties, of new information respecting the rare elements, disclosing their many-sided relations to the other elements and to each other. The researches of Marignac on niobium, and those of Roscoe on vanadium, were of special moment. The striking analogies between vanadium and phosphorus on the one hand, and between vanadium and chromium on the other, which became so apparent in the investigations connected with that element, naturally induced the comparison of $V = 51$ with $Cr = 52$, $Nb = 94$ with $Mo = 96$, and $Ta = 192$ with $W = 194$; while, on the other hand, $P = 31$ could be compared with $S = 32$, $As = 75$ with $Se = 79$, and $Sb = 120$ with $Te = 125$. From such approximations there remained but one step to the discovery of the law of periodicity.

The law of periodicity was thus a direct outcome of the stock of generalisations and established facts which had accumulated by the end of the decade 1860-1870; it is an embodiment of those data in a more or less systematic expression. Where, then, lies the secret of the special importance which has since been attached to the periodic law, and has raised it to the position of a generalisation which has already given to chemistry unexpected aid, and which promises to be far more fruitful in the future and to impress upon several branches of chemical research a peculiar and original stamp? The remaining part of my communication will be an attempt to answer this question.

In the first place we have the circumstance that, as soon as the law made its appearance, it demanded a revision of many facts which were considered by chemists as fully established by existing experience. I shall return, later on, briefly to this subject, but I wish now to remind you that the periodic law, by insisting on the necessity for a revision of supposed facts, exposed itself at once to destruction in its very origin. Its first requirements, however, have been almost entirely satisfied during the last 20 years; the supposed facts have yielded to the law, thus proving that the law itself was a legitimate induction from the verified facts. But our inductions from data have often to do with such details of a science so rich in facts that only generalisations which cover a wide range of important phenomena can attract general attention. What were the regions touched on by the periodic law? This is what we shall now consider.

The most important point to notice is, that periodic functions, used for the purpose of expressing changes which are dependent on variations of time and space, have been long known. They are familiar to the mind when we have to deal with motion in closed cycles, or with any kind of deviation from

² To judge from J. A. R. Newlands's work, *On the Discovery of the Periodic Law*, London, 1884, p. 149; 'On the Law of Octaves' (from the *Chemical News*, 12, 83, August 18, 1865).

a stable position, such as occurs in pendulum-oscillations. A like periodic function became evident in the case of the elements, depending on the mass of the atom. The primary conception of the masses of bodies, or of the masses of atoms, belongs to a category which the present state of science forbids us to discuss, because as yet we have no means of dissecting or analysing the conception. All that was known of functions dependent on masses derived its origin from Galileo and Newton, and indicated that such functions either decrease or increase with the increase of mass, like the attraction of celestial bodies. The numerical expression of the phenomena was always found to be proportional to the mass, and in no case was an increase of mass followed by a recurrence of properties such as is disclosed by the periodic law of the elements. This constituted such a novelty in the study of the phenomena of nature that, although it did not lift the veil which conceals the true conception of mass, it nevertheless indicated that the explanation of that conception must be searched for in the masses of the atoms; the more so as all masses are nothing but aggregations, or additions, of chemical atoms which would be best described as chemical individuals. Let me remark, by the way, that though the Latin word 'individual' is merely a translation of the Greek word 'atom,' nevertheless history and custom have drawn a sharp distinction between the two words, and the present chemical conception of atoms is nearer to that defined by the Latin word than by the Greek, although this latter also has acquired a special meaning which was unknown to the classics. The periodic law has shown that our chemical individuals display an harmonic periodicity of properties dependent on their masses. Now natural science has long been accustomed to deal with periodicities observed in nature, to seize them with the vice of mathematical analysis, to submit them to the rasp of experiment. And these instruments of scientific thought would surely, long since, have mastered the problem connected with the chemical elements, were it not for a new feature which was brought to light by the periodic law, and which gave a peculiar and original character to the periodic function.

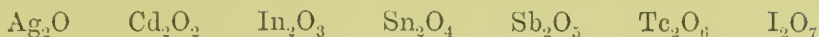
If we mark on an axis of abscissæ a series of lengths proportional to angles, and trace ordinates which are proportional to sines or other trigonometrical functions, we get periodic curves of an harmonic character. So it might seem, at first sight, that with the increase of atomic weights the function of the properties of the elements should also vary in the same harmonious way. But in this case there is no such continuous change as in the curves just referred to, because the periods do not contain the infinite number of points constituting a curve, but a *finite* number only of such points. An example will better illustrate this view. The atomic weights—

Ag = 108	Cd = 112	In = 113	Sn = 118	Sb = 120
	Te = 125	I = 127		

steadily increase, and their increase is accompanied by a modification of many properties which constitutes the essence of the periodic law. Thus, for example, the densities of the above elements decrease steadily, being respectively—

10.5	8.6	7.4	7.2	6.7	6.4	4.9
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while their oxides contain an increasing quantity of oxygen—



But to connect by a curve the summits of the ordinates expressing any of these properties would involve the rejection of Dalton's law of multiple proportions. Not only are there no intermediate elements between silver, which gives AgCl , and cadmium, which gives CdCl_2 , but, according to the very essence of the periodic law, there can be none; in fact, a uniform curve would be inapplicable in such a case, as it would lead us to expect elements possessed of special properties at any point of the curve. The periods of the elements have thus a character very different from those which are so simply represented by geometers. They correspond to points, to numbers, to sudden changes of the masses, and not to a continuous evolution. In these sudden changes destitute of intermediate steps or positions, in the absence of elements intermediate between, say, silver and cadmium, or aluminium and silicon, we must recognise a problem to which no direct application of the analysis of the infinitely small can be made. Therefore, neither the trigonometrical functions proposed by Ridberg and Flavitzky, nor the pendulum-oscillations suggested by Crookes, nor the cubical curves of the Rev. Mr. Haughton, which have been proposed for expressing the periodic law, from the nature of the case, can represent the periods of the chemical elements. If geometrical analysis is to be applied to this subject, it will require to be modified in a special manner. It must find the means of representing in a special way, not only such long periods as that comprising

K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br,

but short periods like the following—



In the theory of numbers only do we find problems analogous to ours, and two attempts at expressing the atomic weights of the elements by algebraic formulæ seem to be deserving of attention, although neither of them can be considered as a complete theory, or as promising finally to solve the problem of the periodic law. The attempt of E. J. Mills (1886) does not even aspire to attain this end. He considers that all atomic weights can be expressed by a logarithmic function,

$$15(n - 0.9375'),$$

in which the variables n and t are *whole numbers*. Thus, for oxygen, $n = 2$, and $t = 1$, whence its atomic weight is $= 15.94$; in the case of chlorine, bromine, and iodine, n has respective values of 3, 6, and 9, whilst $t = 7$, 6, and 9; in the case of potassium, rubidium, and caesium, $n = 4$, 6, and 9, and $t = 14$, 18, and 20.

Another attempt was made in 1888 by B. N. Tchitchérin. Its author places the problem of the periodic law in the first rank, but as yet he has investigated the alkali metals only. Tchitchérin first noticed the simple

relations existing between the atomic volumes of all alkali metals; they can be expressed, according to his views, by the formula

$$A(2 - 0.00535An),$$

where A is the atomic weight, and n is equal to 8 for lithium and sodium, to 4 for potassium, to 3 for rubidium, and to 2 for caesium. If n remained equal to 8 during the increase of A , the volume would become zero at $A = 46\frac{2}{3}$, and it would reach its maximum at $A = 23\frac{1}{3}$. The close approximation of the number $46\frac{2}{3}$ to the differences between the atomic weights of analogous elements (such as Cs—Rb, I—Br, and so on); the close correspondence of the number $23\frac{1}{3}$ to the atomic weight of sodium; the fact of n being necessarily a whole number, and several other aspects of the question, induce Tchitchérin to believe that they afford a clue to the understanding of the nature of the elements; we must, however, await the full development of his theory before pronouncing judgment on it. What we can at present only be certain of is this: that attempts like the two above named must be repeated and multiplied, because the periodic law has clearly shown that the masses of the atoms increase abruptly, by steps, which are clearly connected in some way with Dalton's law of multiple proportions; and because the periodicity of the elements finds expression in the transition from RX to RX_2 , RX_3 , RX_4 , and so on till RX_8 , at which point, the energy of the combining forces being exhausted, the series begins anew from RX to RX_2 , and so on.

While connecting by new bonds the theory of the chemical elements with Dalton's theory of multiple proportions, or atomic structure of bodies, the periodic law opened for natural philosophy a new and wide field for speculation. Kant said that there are in the world 'two things which never cease to call for the admiration and reverence of man: the moral law within ourselves, and the stellar sky above us.' But when we turn our thoughts towards the nature of the elements and the periodic law, we must add a third subject, namely, 'the nature of the elementary individuals which we discover everywhere around us.' Without them the stellar sky itself is inconceivable; and in the atoms we see at once their peculiar individualities, the infinite multiplicity of the individuals, and the submission of their seeming freedom to the general harmony of Nature.

Having thus indicated a new mystery of Nature, which does not yet yield to rational conception, the periodic law, together with the revelations of spectrum analysis, have contributed to again revive an old but remarkably long-lived hope—that of discovering, if not by experiment, at least by a mental effort, the *primary matter*—which had its genesis in the minds of the Grecian philosophers, and has been transmitted, together with many other ideas of the classic period, to the heirs of their civilisation. Having grown, during the times of the alchemists up to the period when experimental proof was required, the idea has rendered good service; it induced those careful observations and experiments which later on called into being the works of Scheele, Lavoisier, Priestley, and Cavendish. It then slumbered awhile, but was soon awakened by the attempts either to confirm or to refute the ideas of Prout as to the multiple-proportion relationship of the atomic

weights of all the elements. And once again the inductive or experimental method of studying Nature gained a direct advantage from the old Pythagorean idea: because atomic weights were determined with an accuracy formerly unknown. But again the idea could not stand the ordeal of experimental test, yet the prejudice remains and has not been uprooted, even by Stas; nay, it has gained a new vigour, for we see that all which is imperfectly worked out, new and unexplained, from the still scarcely studied rare metals to the hardly perceptible nebulae, has been used to justify it. As soon as spectrum analysis appears as a new and powerful weapon of chemistry, the idea of a primary matter is immediately attached to it. From all sides we see attempts to constitute the imaginary substance *helium*³ the so much longed for primary matter. No attention is paid to the circumstance that the helium line is only seen in the spectrum of the solar protuberances, so that its universality in Nature remains as problematic as the primary matter itself; or to the fact that the helium line is wanting amongst the Fraunhofer lines of the solar spectrum, and thus does not answer to the brilliant fundamental conception which gives its real force to spectrum analysis.

And finally, no notice is taken even of the indubitable fact that the brilliancies of the spectral lines of the simple substances vary under different temperatures and pressures; so that all probabilities are in favour of the helium line simply belonging to some long since known element placed under such conditions of temperature, pressure, and gravity as have not yet been realised in our experiments. Again, the idea that the excellent investigations of Lockyer of the spectrum of iron can be interpreted in favour of the compound nature of that element evidently must have arisen from some misunderstanding. The spectrum of a compound certainly does not appear as a sum of the spectra of its components; and therefore the observations of Lockyer can be considered precisely as a proof that iron undergoes no other changes at the temperature of the sun than those which it experiences in the voltaic arc—provided the spectrum of iron is preserved. As to the shifting of some of the lines of the spectrum of iron while the other lines maintain their positions, it can be explained, as shown by M. Kleiber ('Journal of the Russian Chemical and Physical Society,' 1885, 147), by the relative motion of the various strata of the sun's atmosphere, and by Zöllner's laws of the relative brilliancies of different lines of the spectrum. Moreover, it ought not to be forgotten that if iron were really proved to consist of two or more unknown elements, we should simply have an increase in the number of our elements—not a reduction, and still less a reduction of all of them to one single primary matter.

Feeling that spectrum analysis will not yield a support to the Pythagorean conception, its modern promoters are so bent upon its being confirmed by the periodic law that the illustrious Berthelot, in his work '*Les Origines de l'Alchimie*,' 1885, 313, has simply mixed up the fundamental idea of the law of periodicity with the ideas of Prout, the alchemists, and Democritus about primary matter.⁴ But the periodic law, based as it is on the solid and whole-

³ That is, a substance having a wave-length equal to 0.0005875 millimetre.

⁴ He maintains (on p. 309) that the periodic law requires two new analogous elements, having atomic weights of 48 and 64, occupying positions between sulphur

some ground of experimental research, has been evolved independently of any conception as to the nature of the elements; it does not in the least originate in the idea of a unique matter; and it has no historical connection with that relic of the torments of classical thought, and therefore it affords no more indication of the unity of matter or of the compound character of our elements than the law of Avogadro, or the law of specific heats, or even the conclusions of spectrum analysis. None of the advocates of a unique matter have ever tried to explain the law from the standpoint of ideas taken from a remote antiquity when it was found convenient to admit the existence of many gods—and of a unique matter.

When we try to explain the origin of the idea of a unique primary matter, we easily trace that in the absence of inductions from experiment it derives its origin from the scientifically philosophical attempt at discovering some kind of unity in the immense diversity of individualities which we see around. In classical times such a tendency could only be satisfied by conceptions about the immaterial world. As to the material world, our ancestors were compelled to resort to some hypothesis, and they adopted the idea of unity in the formative material, because they were not able to evolve the conception of any other possible unity in order to connect the multifarious relations of matter. Responding to the same legitimate scientific tendency, natural science has discovered throughout the universe a unity of plan, a unity of forces, and a unity of matter, and the convincing conclusions of modern science compel everyone to admit these kinds of unity. But while we admit unity in many things, we none the less must also explain the individuality and the apparent diversity which we cannot fail to trace everywhere. It has been said of old, 'Give us a fulcrum, and it will become easy to displace the earth.' So also we must say, 'Give us something that is individualised, and the apparent diversity will be easily understood.' Otherwise, how could unity result in a multitude?

After a long and painstaking research, natural science has discovered the individualities of the chemical elements, and therefore it is now capable not only of analysing, but also of synthesising; it can understand and grasp generality and unity, as well as the individualised and the multifarious. The general and universal, like time and space, like force and motion, vary uniformly; the uniform admit of interpolations, revealing every intermediate phase. But the multitudinous, the individualised—such as ourselves, or the chemical elements, or the members of a peculiar periodic function of the elements, or Dalton's multiple proportions—is characterised in another way: we see in it, side by side with a connecting general principle, leaps, breaks of continuity, points which escape from the analysis of the infinitely small—an absence of complete intermediate links. Chemistry has found an answer to the question as to the causes of multitudes; and while retaining the conception of many elements, all submitted to the discipline of a general law, it offers an escape from the Indian Nirvana—the absorption in the universal, replacing it by the individualised. However, the place for individuality is so limited by the all-grasping, all-powerful universal,

and selenium, although nothing of the kind results from any of the different readings of the law.

that it is merely a point of support for the understanding of multitude in unity.

Having touched upon the metaphysical bases of the conception of a unique matter which is supposed to enter into the composition of all bodies, I think it necessary to dwell upon another theory, akin to the above conception—the theory of the compound character of the elements now admitted by some—and especially upon one particular circumstance which, being related to the periodic law, is considered to be an argument in favour of that hypothesis.

Dr. Pelopidas, in 1883, made a communication to the Russian Chemical and Physical Society on the periodicity of the hydrocarbon radicles, pointing out the remarkable parallelism which was to be noticed in the change of properties of hydrocarbon radicles and elements when classed in groups. Professor Carnelley, in 1886, developed a similar parallelism. The idea of M. Pelopidas will be easily understood if we consider the series of hydrocarbon radicles which contain, say, 6 atoms of carbon:—

I.	II.	III.	IV.	V.	VI.	VII.	VIII.
C_6H_{13}	C_6H_{12}	C_6H_{11}	C_6H_{10}	C_6H_9	C_6H_8	C_6H_7	C_6H_6

The first of these radicles, like the elements of the first group, combines with Cl, OH, and so on, and gives the derivatives of hexyl alcohol, $C_6H_{13}(OH)$; but, in proportion as the number of hydrogen atoms decreases, the capacity of the radicles of combining with, say, the halogens increases. C_6H_{12} already combines with 2 atoms of chlorine; C_6H_{11} with 3 atoms, and so on. The last members of the series comprise the radicles of acids: thus C_6H_8 , which belongs to the 6th group gives, like sulphur, a bibasic acid, $C_6H_8O_2(OH)_2$, which is homologous with oxalic acid. The parallelism can be traced still further, because C_6H_6 appears as a monovalent radicle of benzene, and with it begins a new series of aromatic derivatives, so analogous to the derivatives of the aliphatic series. Let me also mention another example from among those which have been given by M. Pelopidas. Starting from the alkaline radicle of monomethylammonium, $N(CH_3)H_3$, or NCH_6 , which presents many analogies with the alkaline metals of the 1st group, he arrives, by successively diminishing the number of the atoms of hydrogen, at a 7th group which contains cyanogen, CN, which has long since been compared to the halogens of the 7th group.

The most important consequence which, in my opinion, can be drawn from the above comparison is that the periodic law, so apparent in the elements, has a wider application than might appear at first sight; it opens up a new vista of chemical evolutions. But, while admitting the fullest parallelism between the periodicity of the elements and that of the compound radicles, we must not forget that in the periods of the hydrocarbon radicles we have a *decrease* of mass as we pass from the representatives of the first group to the next, while in the periods of the elements the mass *increases* during the progression. It thus becomes evident that we cannot speak of an identity of periodicity in both cases, unless we put aside the ideas of mass and attraction, which are the real corner-stones of the whole of natural science, and even enter into those very conceptions of simple substances

which came to light a full hundred years later than the immortal principles of Newton.⁵

From the foregoing, as well as from the failures of so many attempts at finding in experiment and speculation a proof of the compound character of the elements and of the existence of primordial matter, it is evident, in my opinion, that this theory must be classed among mere utopias. But utopias can only be combated by freedom of opinion, by experiment, and by new utopias. In the republic of scientific theories freedom of opinions is guaranteed. It is precisely that freedom which permits me to criticise openly the widely diffused idea as to the unity of matter in the elements. Experiments and attempts at confirming that idea have been so numerous that it really would be instructive to have them all collected together, if only to serve as a warning against the repetition of old failures. And now as to new utopias which may be helpful in the struggle against the old ones, I do not think it quite useless to mention a *fantasy* of one of my students who imagined that the weight of bodies does not depend upon their mass, but upon the character of the motion of their atoms. The atoms, according to this new utopian, may all be homogeneous or heterogeneous, we know not which; we know them in motion only, and that motion they maintain with the same persistence as the stellar bodies maintain theirs. The weights of atoms differ only in consequence of their various modes and quantity of motion; the heaviest atoms may be much simpler than the lighter ones: thus an atom of mercury may be simpler than an atom of hydrogen—the manner in which it moves causes it to be heavier. My interlocutor even suggested that the view which attributes the greater complexity to the lighter elements finds confirmation in the fact that the hydrocarbon radicles mentioned by Pelopidas, while becoming lighter as they lose hydrogen, change their properties periodically in the same manner as the elements change theirs, according as the atoms grow heavier.

The French proverb, *La critique est facile, mais l'art est difficile*, however, may well be reversed in the case of all such ideal views, as it is much easier to formulate than to criticise them. Arising from the virgin soil of newly established facts, the knowledge relating to the elements, to their masses, and to the periodic changes of their properties has given a motive for the formation of utopian hypothesis, probably because they could not be foreseen by the aid of any of the various metaphysical systems, and exist, like the idea of gravitation, as an independent outcome of natural science, requiring the acknowledgment of general laws, when these have been established with the same degree of persistence as is indispensable for the acceptance of a thoroughly established fact. Two centuries have elapsed since the theory of gravitation was enunciated, and although we do not understand its cause, we still must regard gravitation as a fundamental conception of natural philosophy, a conception which has enabled us to perceive much more than the metaphysicians did or could with their seeming omniscience. A hundred

⁵ It is noteworthy that the year in which Lavoisier was born (1743)—the author of the idea of elements and of the indestructibility of matter—is later by exactly one century than the year in which the author of the theory of gravitation and mass was born (1643). The affiliation of the ideas of Lavoisier and those of Newton is beyond doubt.

years later the conception of the elements arose ; it made chemistry what it now is ; and yet we have advanced as little in our comprehension of simple substances since the times of Lavoisier and Dalton as we have in our understanding of gravitation. The periodic law of the elements is only twenty years old ; it is not surprising, therefore, that, knowing nothing about the causes of gravitation and mass, or about the nature of the elements, we do not comprehend the *rationale* of the periodic law. It is only by collecting established laws—that is, by working at the acquirement of truth—that we can hope gradually to lift the veil which conceals from us the causes of the mysteries of Nature and to discover their mutual dependency. Like the telescope and the microscope, laws founded on the basis of experiment are the instruments and means of enlarging our mental horizon.

In the remaining part of my communication I shall endeavour to show, and as briefly as possible, in how far the periodic law contributes to enlarge our range of vision. Before the promulgation of this law the chemical elements were mere fragmentary, incidental facts in Nature ; there was no special reason to expect the discovery of new elements, and the new ones which were discovered from time to time appeared to be possessed of quite novel properties. The law of periodicity first enabled us to perceive undiscovered elements at a distance which formerly was inaccessible to chemical vision ; and long ere they were discovered new elements appeared before our eyes possessed of a number of well-defined properties. We now know three cases of elements whose existence and properties were foreseen by the instrumentality of the periodic law. I need but mention the brilliant discovery of *gallium*, which proved to correspond to eka-aluminium of the periodic law, by Lecoq de Boisbaudran ; of *scandium*, corresponding to ekaboron, by Nilson ; and of *germanium*, which proved to correspond in all respects to ekasilicon, by Winkler. When, in 1871, I described to the Russian Chemical Society the properties, clearly defined by the periodic law, which such elements ought to possess, I never hoped that I should live to mention their discovery to the Chemical Society of Great Britain as a confirmation of the exactitude and the generality of the periodic law. Now that I have had the happiness of doing so, I unhesitatingly say that, although greatly enlarging our vision, even now the periodic law needs further improvements in order that it may become a trustworthy instrument in further discoveries.*

I shall venture to allude to some other matters which chemistry has discerned by means of its new instrument, and which it could not have made

* I foresee some more new elements, but not with the same certitude as before. I shall give one example, and yet I do not see it quite distinctly. In the series which contains $\text{Hg} = 204$, $\text{Pb} = 206$, and $\text{Bi} = 208$, we can imagine the existence (at the place VI—11) of an element analogous to tellurium, which we can describe as dvi-tellurium, Dt, having an atomic weight of 212, and the property of forming the oxide DtO_3 . If this element really exists, it ought in the free state to be an easily fusible, crystalline, non-volatile metal of a grey colour, having a density of about 9.3, capable of giving a dioxide, DtO_2 , equally endowed with feeble acid and basic properties. This dioxide must give on active oxidation an unstable higher oxide, DtO_3 , which should resemble in its properties PbO_2 and Bi_2O_5 . Dvi-tellurium hydride, if it be found to exist, will be a less stable compound than even H_2Te . The compounds of dvi-tellurium will be easily reduced, and it will form characteristic definite alloys with other metals.

out without a knowledge of the law of periodicity, and I shall confine myself to simple substances and to oxides.

Before the periodic law was formulated the atomic weights of the elements were purely empirical numbers, so that the magnitude of the equivalent, and the atomicity, or the value in substitution possessed by an atom, could only be tested by critically examining the methods of determination, but never directly by considering the numerical values themselves; in short, we were compelled to move in the dark, to submit to the facts, instead of being masters of them. I need not recount the methods which permitted the periodic law at last to master the facts relating to atomic weights, and I would merely call to mind that it compelled us to modify the valencies of *indium* and *cerium*, and to assign to their compounds a different molecular composition. Determinations of the specific heats of these two metals fully confirmed the change. The trivalency of *yttrium*, which makes us now represent its oxide as Y_2O_3 , instead of as YO , was also foreseen (in 1870) by the periodic law, and it has now become so probable that Clève, and all other subsequent investigators of the rare metals, have not only adopted it, but have also applied it without any new demonstration to substances so imperfectly known as those of the cerite and gadolinite group, especially since Hillebrand determined the specific heats of lanthanum and didymium and confirmed the expectations suggested by the periodic law. But here, especially in the case of didymium we meet with a series of difficulties long since foreseen through the periodic law, but only now becoming evident, and chiefly arising from the relative rarity and insufficient knowledge of the elements which usually accompany didymium.

Passing to the results obtained in the case of the rare elements *beryllium*, *scandium*, and *thorium*, it is found that these have many points of contact with the periodic law. Although Avdeeff long since proposed the magnesia formula to represent beryllium oxide, yet there was so much to be said in favour of the alumina formula, on account of the specific heat of the metals and the isomorphism of the two oxides, that it became generally adopted and seemed to be well established. The periodic law, however, as Brauner repeatedly insisted ('Berichte,' 1878, 872; 1881, 53), was against the formula Be_3O_3 ; it required the magnesia formula BeO —that is, an atomic weight of 9—because there was no place in the system for an element like beryllium having an atomic weight of 13.5. This divergence of opinion lasted for years, and I often heard that the question as to the atomic weight of beryllium threatened to disturb the generality of the periodic law, or, at any rate, to require some important modifications of it. Many forces were operating in the controversy regarding beryllium, evidently because a much more important question was at issue than merely that involved in the discussion of the atomic weight of a relatively rare element: and during the controversy the periodic law became better understood, and the mutual relations of the elements became more apparent than ever before. It is most remarkable that the victory of the periodic law was won by the researches of the very observers who previously had discovered a number of facts in support of the trivalency of beryllium. Applying the higher law of Avogadro, Nilson and Petterson have finally shown that the density of the vapour of the beryl-

lium chloride, BeCl_2 , obliges us to regard beryllium as bivalent in conformity with the periodic law.⁷ I consider the confirmation of Avdeeff's and Brauner's view as important in the history of the periodic law as the discovery of scandium, which, in Nilson's hands, confirmed the existence of ekaboron.

The circumstance that *thorium* proved to be quadrivalent, and $\text{Th} = 232$, in accordance with the views of Chydenius and the requirements of the periodic law, passed almost unnoticed, and was accepted without opposition, and yet both thorium and uranium are of great importance in the periodic system, as they are its last members, and have the highest atomic weights of all the elements.

The alteration of the atomic weight of *uranium* from $\text{U} = 120$ into $\text{U} = 240$ attracted more attention, the change having been made on account of the periodic law, and for no other reason. Now that Rosee, Rammelsberg, Zimmermann, and several others have admitted the various claims of the periodic law in the case of uranium, its high atomic weight is received without objection, and it endows that element with a special interest.

While thus demonstrating the necessity for modifying the atomic weights of several insufficiently known elements, the periodic law enabled us also to detect errors in the determination of the atomic weights of several elements whose valencies and true position among other elements were already well known. Three such cases are especially noteworthy: those of tellurium, titanium, and platinum. Berzelius had determined the atomic weight of *tellurium* to be 128, while the periodic law claimed for it an atomic weight below that of iodine, which had been fixed by Stas at 126.5, and which was certainly not higher than 127. Brauner then undertook the investigation, and he has shown that the true atomic weight of tellurium is lower than that of iodine, being near to 125. For *titanium*, the extensive researches of Thorpe have confirmed the atomic weight of $\text{Ti} = 48$, indicated by the law and already foreseen by Rose, but contradicted by the analyses of Pierre and several other chemists. An equally brilliant confirmation of the expectations based on the periodic law has been given in the case of the series osmium, iridium, platinum, and gold. At the time of the promulgation of the periodic law, the determinations of Berzelius, Rose, and many others gave the following figures:—

$\text{Os} = 200$; $\text{Ir} = 197$; $\text{Pt} = 198$; $\text{Au} = 196$.

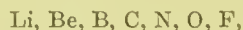
⁷ Let me mention another proof of the bivalency of beryllium which may have passed unnoticed, as it was only published in the Russian chemical literature. Having remarked (in 1884) that the density of such solutions of chlorides of metals, MCl_n , as contain 200 mols. of water (or a large and constant amount of water) regularly increases as the molecular weight of the dissolved salt increases, I proposed to one of our young chemists, M. Burdakoff, that he should investigate beryllium chloride. If its molecule be BeCl_2 its weight must be $= 80$; and in such a case it must be heavier than the molecule of $\text{KCl} = 74.5$, and lighter than that of $\text{MgCl}_2 = 93$. On the contrary, if beryllium chloride is a trichloride, $\text{BeCl}_3 = 120$, its molecule must be heavier than that of $\text{CaCl}_2 = 111$, and lighter than that of $\text{MnCl}_2 = 126$. Experiment has shown the correctness of the former formula, the solution $\text{BeCl}_2 + 200\text{H}_2\text{O}$ having (at $15^\circ/4^\circ$) a density of 1.0138, this being a higher density than that of the solution $\text{KCl} + 200\text{H}_2\text{O}$ ($= 1.0121$), and lower than that of $\text{MgCl}_2 + 200\text{H}_2\text{O}$ ($= 1.0203$). The bivalency of beryllium was thus confirmed in the case of both the dissolved and the vaporised chloride.

The expectations of the periodic law⁸ have been confirmed, first, by new determinations of the atomic weight of *platinum* (by Seubert, Dittmar, and M'Arthur, which proved to be near to 196 (taking O = 16, as proposed by Marignac, Brauner, and others); secondly, by Seubert having proved that the atomic weight of *osmium* is really lower than that of platinum, being near to 191; and thirdly, by the investigations of Krüss, Thorpe, and Laurie, proving that the atomic weight of *gold* exceeds that of platinum, and approximates to 197. The atomic weights which were thus found to require correction were precisely those which the periodic law had indicated as affected with errors; and it has been proved, therefore, that the periodic law affords a means of testing experimental results. If we succeed in discovering the exact character of the periodic relationships between the increments in atomic weights of allied elements discussed by Ridberg in 1885, and again by Bazaroff in 1887, we may expect that our instrument will give us the means of still more closely controlling the experimental data relating to atomic weights.

Let me next call to mind that, while disclosing the variation of chemical properties,⁹ the periodic law has also enabled us to systematically discuss many of the physical properties of elementary bodies, and to show that these properties are also subject to the law of periodicity. At the Moscow Congress of Russian Naturalists in August 1869 I dwelt upon the relations which existed between density and the atomic weight of the elements. The following year Professor Lothar Meyer, in his well-known paper,¹⁰ studied the same subject in more detail, and thus contributed to spread information about the periodic law. Later on, Carnelley, Laurie, L. Meyer, Roberts-Austen, and several others applied the periodic system to represent the order in the changes of the magnetic properties of the elements, their melting-points, the heats of formation of their haloid compounds, and even of such mechanical properties as the coefficient of elasticity, the breaking stress, &c., &c. These deductions, which have received further support in the discovery of new elements endowed not only with chemical but even with physical properties, which were foreseen by the law of periodicity, are well known; so I need not dwell upon the subject, and may pass to the consideration of oxides.¹¹

⁸ I pointed them out in the *Liebig's Annalen*, Supplement Band viii. 1871, p. 211.

⁹ Thus, in the typical small period of



we see at once the progression from the alkali metals to the acid non-metals, such as are the halogens.

¹⁰ *Liebig's Annalen*, Supplement Band vii. 1870.

¹¹ A distinct periodicity can also be discovered in the spectra of the elements. Thus the researches of Hartley, Ciamician, and others have disclosed, first, the homology of the spectra of analogous elements; secondly, that the alkali metals have simpler spectra than the metals of the following groups; and thirdly, that there is a certain likeness between the complicated spectra of manganese and iron on the one hand, and the no less complicated spectra of chlorine and bromine on the other hand, and their likeness corresponds to the degree of analogy between those elements which is indicated by the periodic law.

In indicating that the gradual increase of the power of elements of combining with oxygen is accompanied by a corresponding decrease in their power of combining with hydrogen, the periodic law has shown that there is a limit of oxidation, just as there is a well-known limit to the capacity of elements for combining with hydrogen. A single atom of an element combines with at most four atoms of either hydrogen or oxygen; and while CH_4 and SiH_4 represent the highest hydrides, so RuO_4 and OsO_4 are the highest oxides. We are thus lead to recognise types of oxides, just as we have had to recognise types of hydrides.¹²

The periodic law has demonstrated that the maximum extent to which different non-metals enter into combination with oxygen is determined by the extent to which they combine with hydrogen, and that the sum of the number of equivalents of both must be equal to 8. Thus chlorine, which combines with 1 atom or 1 equivalent of hydrogen, cannot fix more than 7 equivalents of oxygen, giving Cl_2O_7 ; while sulphur, which fixes 2 equivalents of hydrogen, cannot combine with more than 6 equivalents or 3 atoms of oxygen. It thus becomes evident that we cannot recognise as a fundamental property of the elements the atomic valencies deduced from their hydrides; and that we must modify, to a certain extent, the theory of atomicity if we desire to raise it to the dignity of a general principle capable of affording an insight into the constitution of all compound molecules. In other words, it is only to carbon, which is quadrivalent with regard both to oxygen and hydrogen, that we can apply the theory of constant valency and of bond, by means of which so many still endeavour to explain the structure of compound molecules. But I should go too far if I ventured to explain in detail the conclusions which can be drawn from the above considerations. Still, I think it necessary to dwell upon one particular fact which must be explained from the point of view of the periodic law in order to clear the way to its extension in that particular direction.

The higher oxides yielding salts the formation of which was foreseen by the periodic system—for instance, in the short series beginning with sodium—

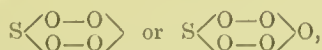


must be clearly distinguished from the higher degrees of oxidation which correspond to hydrogen peroxide and bear the true character of peroxides. Peroxides such as Na_2O_2 , BaO_2 , and the like have long been known. Similar

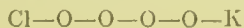
¹² Formerly it was supposed that, being a bivalent element, oxygen can enter into any grouping of the atoms, and there was no limit foreseen as to the extent to which it could further enter into combination. We could not explain why bivalent sulphur, which forms compounds such as



could not also form oxides such as—



while other elements, as, for instance, chlorine, form compounds such as —



peroxides have also recently become known in the case of chromium, sulphur, titanium, and many other elements, and I have sometimes heard it said that discoveries of this kind weaken the conclusions of the periodic law in so far as it concerns the oxides. I do not think so in the least, and I may remark, in the first place, that all these peroxides are endowed with certain properties obviously common to all of them, which distinguish them from the actual, higher, salt-forming oxides, especially their easy decomposition by means of simple contact agencies; their incapability of forming salts of the common type; and their capability of combining with other peroxides (like the faculty which hydrogen peroxide possesses of combining with barium peroxide, discovered by Schöene). Again, we remark that some groups are especially characterised by their capacity of generating peroxides. Such is, for instance, the case in the sixth group, where we find the well-known peroxides of sulphur, chromium, and uranium; so that further investigation of peroxides will probably establish a new periodic function, foreshadowing that molybdenum and tungsten will assume peroxide forms with comparative readiness. To appreciate the constitution of such peroxides, it is enough to notice that the peroxide form of sulphur (so-called persulphuric acid) stands in the same relation to sulphuric acid as hydrogen peroxide stands to water:—



and so also—



Similar relations are seen everywhere, and they correspond to the principle of substitutions which I long since endeavoured to represent as one of the chemical generalisations called into life by the periodic law. So also sulphuric acid, if considered with reference to hydroxyl, and represented as follows—



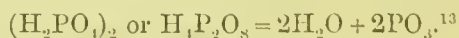
has its corresponding compound in dithionic acid—



Therefore, also, phosphoric acid, $\text{HO}(\text{POH}_2\text{O}_2)$, has, in the same sense, its corresponding compound in the subphosphoric acid of Saltzer:—



and we must suppose that the peroxide compound corresponding to phosphoric acid, if it be discovered, will have the following structure:—



So far as is known at present, the highest form of peroxides is met with in

¹³ In this sense, oxalic acid, $(\text{COOH})_2$, also corresponds to carbonic acid, $\text{OH}(\text{COOH})$, in the same way that dithionic acid corresponds to sulphuric acid, and subphosphoric acid to phosphoric; hence, if a peroxide corresponding to carbonic acid be obtained, it will have the structure of $(\text{HCO}_3)_2$, or $\text{H}_2\text{C}_2\text{O}_6 = \text{H}_2\text{O} + \text{C}_2\text{O}_5$. So also lead must have a real peroxide, Pb_2O_5 .

the peroxide of uranium, UO_4 , prepared by Fairley;¹⁴ while OsO_4 is the highest oxide giving salts. The line of argument which is inspired by the periodic law, so far from being weakened by the discovery of peroxides, is thus actually strengthened, and we must hope that a further exploration of the region under consideration will confirm the applicability to chemistry generally of the principles deduced from the periodic law.

Permit me now to conclude my rapid sketch of the oxygen compounds by the observation that the periodic law is especially brought into evidence in the case of the oxides which constitute the immense majority of bodies at our disposal on the surface of the earth.

The oxides are evidently subject to the law, both as regards their chemical and their physical properties, especially if we take into account the cases of polymerism which are so obvious when comparing CO_2 with Si_nO_{2n} . In order to prove this I give the densities s and the specific volumes v of the higher oxides of two short periods. To render comparison easier, the oxides are all represented as of the form R_2O_n . In the column headed Δ the differences are given between the volume of the oxygen compound and that of the parent element divided by n —that is, by the number of atoms of oxygen in the compound:¹⁵—

	s .	v .	Δ		s .	v .	Δ
Na_2O	2.6	24	-22	K_2O	2.7	35	-55
Mg_2O_2	3.6	22	- 3	Ca_2O	3.15	36	- 7
Al_2O_3	4.0	26	+ 1.3	Sc_2O_3	3.86	35	0
Si_2O_4	2.65	45	5.2	Li_2O_4	4.2	38	+ 5
P_2O_5	2.39	59	6.2	V_2O_5	3.49	52	6.7
S_2O_6	1.96	82	8.7	Cr_2O_6	2.74	73	9.5

I have nothing to add to these figures, except that like relations appear in other periods as well. The above relations were precisely those which made it possible for me to be certain that the relative density of ekasilicon oxide would be about 4.7; germanium oxide, actually obtained by Winkler, proved, in fact, to have the relative density 4.703.

The foregoing account is far from being an exhaustive one of all that has already been discovered by means of the periodic law telescope in the boundless realms of chemical evolution. Still less is it an exhaustive account of all that may yet be seen, but I trust that the little which I have said will account for the philosophical interest attached in chemistry to this law. Although

¹⁴ The compounds of uranium prepared by Fairley seem to me especially instructive in understanding the peroxides. By the action of hydrogen peroxide on uranium oxide, UO_3 , a peroxide of uranium, $\text{UO}_4 \cdot 4\text{H}_2\text{O}$, is obtained ($\text{U} = 240$) if the solution be acid; but if hydrogen peroxide act on uranium oxide in the presence of caustic soda, a crystalline deposit is obtained which has the composition $\text{Na}_4\text{UO}_3 \cdot 4\text{H}_2\text{O}$, and evidently is a combination of sodium peroxide, Na_2O_2 , with uranium peroxide, UO_4 . It is possible that the former peroxide, $\text{UO}_4 \cdot 4\text{H}_2\text{O}$, contains the elements of hydrogen peroxide and uranium peroxide, U_2O_7 , or even $\text{U}(\text{OH})_6 \cdot \text{H}_2\text{O}_2$, like the peroxide of tin recently discovered by Spring, which has the constitution $\text{Sn}_2\text{O}_5 \cdot \text{H}_2\text{O}_2$.

¹⁵ Δ thus represents the average increase of volume for each atom of oxygen contained in the higher salt-forming oxide. The acid oxides give, as a rule, a higher value of Δ , while in the case of the strongly alkaline oxides its value is usually negative.

but a recent scientific generalisation, it has already stood the test of laboratory verification, and appears as an instrument of thought which has not yet been compelled to undergo modification ; but it needs not only new applications but also improvements, further development, and plenty of fresh energy. All this will surely come, seeing that such an assembly of men of science as the Chemical Society of Great Britain has expressed the desire to have the history of the periodic law described in a lecture dedicated to the glorious name of Faraday.

APPENDIX III

AN ATTEMPT TOWARDS A CHEMICAL CONCEPTION OF THE ETHER

By PROFESSOR D. MENDELÉEFF

IN his 'Dictionnaire Complet,' P. Larousse defines the ether as 'an imponderable elastic fluid, filling space and forming the source of light, heat, electricity, &c.' This is laconic, but sufficient to raise some misgivings in the mind of a thoughtful man of science. He is obliged to admit, in the ether, the properties of a substance (fluid), while at the same time, in order to explain in some way the transmission of energy through space by its motion, the ether is assumed to be an all-pervading 'medium.' Moreover, in order to explain the phenomena of light, electricity, and even gravity, this medium is supposed to undergo various disturbances (perturbations) and changes in its structure (deformation), like those observed in solids, liquids, and gases. If the fluid medium permeates everything and everywhere, it cannot be said to have weight, just as the ponderability of air could not be recognised before the invention of the air-pump. Yet the ether must have weight, because, since the days of Galileo and Newton, the quality of gravitation or of weight forms a primary property of substances. From various considerations Lord Kelvin came to the conclusion that a cubic metre of ether should weigh about and not less than 0.000,000,000,000,000,1 gm., while a cubic metre of the lightest gas, hydrogen, weighs 90 grams under the atmospheric pressure. The above-mentioned misgivings of the thoughtful scientist begin in his most plausible endeavours to ascribe a certain weight or mass to the ether, for the question naturally arises: At what pressure and temperature will this weight be proper to ether? For at infinitely small pressures or exceedingly high temperatures, steam or hydrogen would have as small a density as that given by Lord Kelvin for the ether. And as regards the density of the ether in interplanetary space, neither steam nor hydrogen would have a measurable density in these regions, notwithstanding the extreme cold, for the pressure would be infinitely small. Theoretically, space may be supposed to be filled with such rarefied residues of vapours and gases. And this view even corresponds with Kant's and Laplace's and other theories, which strive

to explain the unity of plan in the creation of the heavenly bodies. It also accounts for the uniformity of the chemical composition of the entire universe, demonstrated by the spectroscope, as it gives a means, through the agency of such ether, of interchange between the heavenly bodies. One of the objects of an investigation into the elasticity or compressibility of gases under low pressure, undertaken by me in the seventies, was to trace, as far as the then existing methods of measuring low pressures permitted, the changes proceeding in gases under low pressures. The discrepancies from Boyle's law observed (by me and M. Kirpichnikoff, 1874) for all gases, and subsequently confirmed by Ramsay and others (although still denied by some investigators), indicate a certain uniformity in the behaviour of all gases and a tendency in them towards a certain limiting expansion at low pressures, just as there is a limit to compression (liquefaction and the critical state). But determinations of very low pressures are accompanied by insurmountable difficulties. It proved practically impossible to measure, with any degree of accuracy, pressures under tenths of a millimetre of mercury, and this is far too large a figure for such rarefied media as are supposed to exist at an elevation of even 50 kilometres above the sea level. Hence the conception of the ether as a highly rarefied atmospheric gas cannot so far be subjected to experimental investigation and measurement, which alone can direct the mind in the right direction and lead to reliable results.

But, beyond this, the conception of the ether as a limiting state of expansion of vapours and gases cannot sustain even the most elementary analysis, for ether cannot be understood otherwise than as an all-pervading ubiquitous substance, and this is not the property of either gases or vapours. Both the latter are liquefiable under pressure, and cannot be said to permeate all substances, although they are widely distributed in nature, even in meteorites. Moreover—and this is most important—they vary infinitely in their chemical nature and in their relations to other substances, while the ether, as far as is known, is invariable. Owing to the variety of their chemical properties, all vapours and gases should react differently on the bodies which they permeate if they were components of the ether.

Before proceeding further, I think it necessary to justify the chemical views here and elsewhere brought into play. In the days of Galileo and Newton it was possible, although difficult, to conceive ether apart from them. But now it would be contrary to the most fundamental principles of natural science, for chemistry, since Lavoisier, Dalton, and Avogadro Gerhardt, has acquired the most sacred rights of citizenship in the great company of the natural sciences, and by placing the mass (weight) of a substance among its paramount conceptions it has followed the path indicated by Galileo and Newton. Moreover, chemistry and its methods alone have promoted in science a desire to apprehend bodies and their phenomena in their ultimate relations, through a conception of the reaction of their infinitely small parts or atoms, which may in fact be regarded as indivisible individuals, having nothing in common with the mechanically indivisible atoms of the ancient metaphysicians. There are many proofs of this; it will suffice to mention the fact that the atoms of modern science have often been explained by vortex

rings ; that there was formerly a strong inclination to conceive the chemical atoms as built up of themselves, or of a 'primary matter' ; and that recently, especially in speaking of the radio-active substances, a division of chemical atoms into yet smaller 'electrons' begins to be recognised—all of which would be logically impossible were the atom regarded as mechanically indivisible. Chemically the atoms may be likened to the heavenly bodies, the stars, sun, planets, satellites, comets, &c. The building up of molecules from atoms, and of substances from molecules, is then conceived to resemble the building up of systems, such as the solar system, or that of twin stars or constellations, from these individual bodies. This is not a simple play of words in modern chemistry, nor a mere analogy, but a reality which directs the course of all chemical research, analysis, and synthesis. Chemistry has its own microscope for investigating invisible regions, and being an archi-real science it deals all the time with its invisible individualities without considering them mechanically indivisible. The atoms and molecules which are dealt with in all provinces of modern mechanics and physics cannot be other than the atoms and molecules defined by chemistry, for this is required by the unity of science. And therefore the metaphysicians of the present day should, for the advancement of knowledge, regard atoms in the same sense as that in which they are understood by natural science and not after the manner of the ancient metaphysicians of the Chinese or Greek school. If the Newtonian theory of gravity revealed the existence of forces acting at infinitely great distances, the chemistry of Lavoisier, Dalton, and Avogadro Gerhardt, on the other hand, disclosed the existence of forces of immense power acting at infinitely small distances, and transmutable into all other forms of energy, mechanical and physical. Thus all the present-day fundamental conceptions of natural science—and consequently the conception of the ether—must necessarily be considered under the combined influence of chemical, physical, and mechanical teachings. Although sceptical indifference is prone to discern only a 'working hypothesis' in the conception of the ether, yet the earnest investigator, seeking the reality of truth, and not the image of fantasy, is forced to ask himself what is the chemical nature of the ether.

Before endeavouring to give an answer respecting the chemical nature of ether, I think it necessary to state my opinion regarding the belief held by some in the unity of the substance of the chemical elements and their origin from one primary form of matter. According to this view, ether consists of this primary matter in an unassociated form, that is, not in the form of the elementary atoms or molecules of substances, but as the constituent principle out of which the chemical atoms are formed. This view has much that is attractive. The atoms are regarded as proceeding from primary matter in the same way as celestial bodies are sometimes represented as being formed from disunited bodies, such as cosmic dust, &c. The celestial bodies so formed remain surrounded by the cosmic dust, &c., from which they took their origin. So also the atoms remain in the midst of the all-pervading and primary ether from which they took their origin. Some persons assume also that atoms can be split up into their dust or primary matter, just as comets break up into falling stars ; and that as the geological changes of the

earth or the building up and association of heavenly bodies proceed before our eyes, so also do the atoms break up and form again in the silence of their eternal evolution. Others, without denying the possibility of such a process in exceptional, rare cases, consider the world of atoms to have been established once for all, and do not admit the possibility of decomposing the atom into its primary matter, or of forming new atoms of any chemical element from this primary matter by experimental means. In a word, they regard the process of the creation of atoms as finite and not subject to repetition, while they consider the ether as the residue remaining after the formation of atoms. This view need not be considered here, it being solely the fruit of imagination and unproved by any experimental investigation. But the former theory of a progressive evolution of the substance of atoms cannot be passed unnoticed by chemistry, for fundamental principles of this science are the indestructibility of matter and the immutability of the atoms forming the elements. If ether were producible from atoms and atoms could be built up from ether, the formation of new unlooked-for atoms and the disappearance of portions of the elements during experiment would be possible. A belief in such a possibility has long been held in the minds of many by force of superstition; and the more recent researches of Emmens to convert silver into gold, and those of Fittica (1900) to prove that phosphorus can be transformed into arsenic, show that it yet exists. In the fifty years during which I have carefully followed the records of chemistry, I have met with many such instances, but they have always proved unfounded. It is not my purpose here to defend the independent individuality of the chemical elements, but I am forced to refer to it in speaking of the ether, for it seems to me that, besides being chemically invalid, it is impossible to conceive of ether as a primary substance, because such a substance should have some mass or weight and also chemical relations—mass in order to explain the majority of phenomena proceeding at all distances up to the infinitely great, and chemical relations in order to explain those proceeding at distances infinitely small or commensurable with the atoms. If the question were restricted to the ether which fills space and serves as a medium for the transmission of energy, it would in a way be possible to limit oneself to the supposition of mass without reference to its chemical relations and even to consider the ether as a primary matter, just as the mass of a planet may be conceived without regarding its chemical composition. But such an indifferent, indefinite ether loses all sense of reality and awakens the misgivings of the earnest investigator, directly he realises that it must permeate all substances. The necessity of an easy and perfect permeation of all bodies by the ether has to be admitted, not only for the comprehension of many physical phenomena (such as those of optics), but also owing to the great elasticity and rarity of the ethereal substance, the atoms of which are always conceived as being far more minute than the atoms and molecules of the known chemical substances. Moreover, this permeability of ether in all bodies explains why it cannot be isolated from substances, which indeed behave in respect to ether like a sieve to water or air. The capacity of the ether to penetrate all substances may, however, be regarded as the ideal of the diffusion of gases through metals and other diaphragms. Hydrogen,

which has a small atomic weight and is the slightest of all known gases, not only diffuses more rapidly than any other gas, but also has the faculty of penetrating through walls of such metals as platinum and palladium, which are impervious to other gases. This property is certainly due, not only to the rapidity of the motion of the molecules of hydrogen, closely connected with its small density, but also to a chemical faculty of the same kind as is exhibited in the formation of metallic hydrides, of solutions, alloys, and other indefinite compounds. The mechanism of this penetration may be likened (at the surface of the body penetrated) to the solution of a gas in a liquid, that is, to the gaseous particles leaping into the interstices between the particles of the liquid with a retardation of their motion (a partial liquefaction of the gas), and a bringing into harmony of the motion of both kinds of particles. The condensed gas absorbed at the surface of contact travels in all directions through the body, and diffuses from one layer to another until it entirely permeates it. The possibility of gaseous hydrogen acting thus is evident from the fact that even gold diffuses through solid lead under the same force. At length, at the opposite surface of the body penetrated, the condensed gas will find it possible to escape into greater freedom, and will continue to pass in this direction until its degree of concentration becomes the same on both sides. When this takes place it does not set up a state of rest, but one of mobile equilibrium, that is, equal numbers of molecules or atoms will escape and leap in on the two sides. If, as it must, ether have the faculty of permeating all substances, it must be even lighter and more elastic (greater *vis viva*) than hydrogen, and, what is most important, must have a less capacity than hydrogen to form chemical compounds with the bodies it permeates. Compounds are characterised by the fact that the diverse atoms in them form systems or molecules, in which the different elements are in compatible, harmonious motion. We must therefore suppose that such a state of harmonious motion, of, for instance, hydrogen and palladium, is actually set up in those atoms of hydrogen which permeate the palladium, and that in so doing it forms with the palladium some compound (either Pd_2H or another) which easily dissociates when heated. Hence it seems to me that the atoms of ether are so void of this faculty of forming compounds (which is already weak in hydrogen) that such compounds dissociate at all temperatures, and that therefore nothing beyond a certain condensation among the atoms of substances can be looked for in the ether.

Eight years ago it would have been most arbitrary to deny the existence, in the substance or atoms of ether, of the faculty of forming any compounds with other chemical elements, for in those days all the known elements were, directly or indirectly, capable of entering into mutual combination. But in 1894 Lord Rayleigh and Professor Ramsay discovered argon, and defined it as the most inactive element; this was followed by the discovery of helium, the existence of which Lockyer had predicted by its spectrum as a solar element, and subsequently by the separation of neon, krypton, and xenon from air. None of these five new gases have yet given any definite compounds, although they clearly evince the faculty of solution, i.e., of forming indefinite, easily dissociated compounds. Thus we have now every

right to say that the ether is unable to form any stable compounds with other chemical atoms, although it permeates all substances.

Hence *the ether may be said to be a gas, like helium or argon, incapable of chemical combination*. This definition of ether requires further consideration. The recognition of the ether as a gas signifies that it belongs to the category of the ordinary physical states of matter, gaseous, liquid, and solid. It does not require the recognition of a peculiar fourth state beyond the human understanding (Crookes). All mystical, spiritual ideas about ether disappear. In calling ether a gas, we understand a 'fluid' in the widest sense; an elastic fluid having no cohesion between its parts. Furthermore, if ether be a gas, it has weight; this is indisputable, unless the whole essence of natural science, from the days of Galileo, Newton, and Lavoisier, be discarded for its sake. But since ether possesses so great a penetrative power that it passes through every envelope, it is, of course, impossible to determine experimentally its mass in a given amount of other substances, or the weight of a given volume of ether. We ought, therefore, not to speak of the imponderability of ether, but only of the impossibility of weighing it.

The preceding remarks are in exact accordance with the generally accepted conception of ether. The only addition made is to ascribe to ether the properties of a gas, like argon and helium, utterly incapable of entering into true chemical combination. This point lies at the basis of our investigation into the chemical nature of ether, and includes the following two fundamental propositions: (1) that the ether is the lightest (in this respect ultimate) gas, and is endowed with a high penetrating power, which signifies that its particles have, relatively to other gases, small weight and extremely high velocity; and (2) that ether is a simple body (element) incapable of entering into combination or reaction with other elements or compounds, although capable of penetrating their substance, just as helium, argon, and their analogues are soluble in water and other liquids.

The argon group of gases and the periodic system of the elements have such a close bearing upon our further consideration of the chemical nature of ether that it behoves us to look at them more closely.

When in 1869 I first showed the periodic dependence of the properties of the elements upon their atomic weights, no element incapable of forming definite compounds was known, nor was the existence of such an element even suspected. Therefore the periodic system was arranged by me in groups, series, and periods, starting in group I. and series I., with hydrogen as the lightest and least dense of all the elements. It never occurred to me that hydrogen might be the starting-point of a system of elements. Guided by this system, I was able to predict both the existence of several unknown elements and also their physical and chemical properties in a free and combined state. These elements, gallium, scandium, and germanium, were subsequently discovered by Lecoq de Boisbaudran, Nilson, and Winkler respectively. I made these predictions by following what is known in mathematics as a method of interpolation, that is, by finding intermediate points by means of two extreme points whose relative position is known. The fact of my predictions having proved true confirmed the periodic

system of the elements, which may now be considered as an absolute law. So long as the law remained unconfirmed, it was not possible to extrapolate (i.e., to determine points beyond the limits of the known) by its means; but now such a method may be followed, and I have ventured to do so in the following remarks on the ether, as an element lighter than hydrogen. My reason for doing this was determined by two considerations. In the first place, I think I have not many years for delay; and, in the second place, in recent years there has been much talk about the division of atoms into more minute electrons, and it seems to me that such ideas are not so much metaphysical as metachemical, proceeding from the absence of any definite notions upon the chemism of ether, and it is my desire to replace such vague ideas by a more real notion of the chemical nature of the ether. For until someone demonstrates either the actual transformation of ordinary matter into ether, or the reverse, or else the transformation of one element into another, I consider that any conception of the division of atoms is contrary to the scientific teaching of the present day; and that those phenomena in which a division of atoms is recognised would be better understood as a separation or emission of the generally recognised and all-permeating ether. In a word, it seems to me that the time has arrived to speak of the chemical nature of ether, all the more so since, so far as I know, no one has spoken at all definitely on this subject. When I applied the periodic law to the analogues of boron, aluminium, and silicon, I was thirty-three years younger than now, and I was perfectly confident that sooner or later my prediction would be fulfilled. Now I see less clearly and my confidence is not so great. Then I risked nothing, now I do. This required some courage, which I acquired when I saw the phenomena of radio-activity. I then saw that I must not delay, that perhaps my imperfect thoughts might lead someone to a surer path than that which was opened to my enfeebled vision.

First, I shall treat of the position of helium, argon, and their analogues in the periodic system; then of the position of ether in this system; and conclude with some remarks on the probable properties of ether according to the position it occupies in the periodic system.

When, in 1895, I first heard of argon and its great chemical inertness, I doubted the elementary nature of the gas, and thought it might be a polymeride of nitrogen, N_3 , just as ozone, O_3 , is a polymeride of oxygen, with the difference that, while ozone is formed from oxygen with the absorption of heat, argon might be regarded as nitrogen deprived of heat. In chemistry nitrogen was always regarded as the type of chemical inertness, i.e., of an element which enters into reaction with great difficulty, and if its atoms lost heat in becoming condensed by polymerisation from N_2 to N_3 , it would form a still less active body; just as silica, which is formed from silicon and oxygen with the evolution of heat, is more inert than either of them separately. Berthelot subsequently published a similar view on the nature of argon, but I have now long discarded this, and consider argon to be an independent element, as Ramsay held it to be from the very beginning. Many reasons induced me to adopt this view, and chiefly the facts that (1) the density of argon is certainly much below 21, namely, about 19, that

of H being 1, while the density of N_3 would be about 21, for the molecular weight of $N_3 = 14 \times 3 = 42$, and the density should be half this; (2) helium, discovered by Ramsay in 1895, has a density of about 2 referred to hydrogen, and exhibits the same chemical inactivity as argon, and in its case this inactivity can certainly not be due to a complexity of its molecule; (3) in their newly discovered neon, krypton, and xenon, Ramsay and Travers found a similar inactivity which, in these cases also, could not be explained by polymerisation; (4) the independent nature of the separate spectra of these gases and the invariability of these spectra under the influence of electric sparks proved that they belong to a family of elementary gases different from all other elements; and (5) the graduation and definite character of the physical properties in dependence upon the density and atomic weight further confirm the fact of their being simple bodies, whose individuality, in the absence of chemical reactions, can only be affirmed from the constancy of their physical features. An instance of this is seen in the boiling-points (at 760 mm.) or temperatures at which the vapour pressures equal the atmospheric pressure, and at which the liquid and gaseous phases are co-existent:

—	Helium	Neon	Argon	Krypton	Xenon
Atomic weight . . .	4	19.9	38	81.8	128
Observed density . . .	2	9.95	18.8	40.6	63.5
Observed boiling-point .	-262°	-239°	-187°	-152°	-100°

This recalls the halogen group:

—	Fluorine	Chlorine	Bromine	Iodine
Molecular weight	38	79.9	159.9	254
Vapour density	19	35.5	80	127
Boiling-point	-187°	-34°	+57.7°	+183.7°

In both cases the boiling-point clearly rises with the atomic or molecular weight. When the elementary nature of the argon analogues and their characteristic chemical inactivity were once proved, it became essential that they should take their place in the periodic system of the elements; not in any of the known groups, but in a special one of their own, for they exhibited new, hitherto unknown chemical properties, and the periodic system embraces in different groups those elements which are analogous in their fundamental chemical properties, although not in dependence upon these properties but upon their atomic weight, which apparently—previous to the discovery of the periodic law—stands in no direct relation to these properties. This was a critical test for the periodic law and the analogues of argon, but they both stood the test with perfect success; that is, the atomic weights, calculated from the observed densities, proved to be in perfect accordance with the periodic law.

Although I assume that the reader is acquainted with the periodic law, yet it may be well to mention that if the elements be arranged in the order

of their atomic weights it will be found that similar variations in their chemical properties repeat themselves periodically, and that the order of the faculty of the elements to combine with other elements also corresponds with the order of their atomic weights. This is seen in the following simple example.

All the elements having an atomic weight of not less than 7 and not more than 35.5 fall into two series :

Li = 7.0	Be = 9.1	B = 11.0	C = 12.0	N = 14.0	O = 16	F = 19.0
Lithium	Beryllium	Boron	Carbon	Nitrogen	Oxygen	Fluorine
Na = 23.0	Mg = 24.3	Al = 27.0	Si = 28.4	P = 31.0	S = 32.1	Cl = 35.5
Sodium	Magnesium	Aluminium	Silicon	Phosphorus	Sulphur	Chlorine

Each pair of elements present a great similarity in their chief properties ; this is especially marked in the higher saline oxides, which in the lower series are :



or



Thus the atomic order of the elements exactly corresponds to the arithmetical order from 1 to 7. So that the groups of the analogous elements may be designated by the Roman eiphers I. to VII. ; and when it is said that phosphorus belongs to group V., it signifies that it forms a higher saline oxide, P_2O_5 . And if the analogues of argon do not form any compounds of any kind, it is evident that they cannot be included in any of the groups of the previously known elements, but should form a special zero group which at once expresses the fact of their chemical indifference. Moreover, their atomic weight should necessarily be less than those of group I. : Li, Na, K, Rb, and Cs, but greater than those of the halogens, F, Cl, Br, and I, and this *a priori* conclusion was subsequently confirmed by fact, thus :

Halogens	Argon analogues	Alkali metals
	He = 4.0	Li = 7.03
F = 19	Ne = 19.9	Na = 23.05
Cl = 35.5	Ar = 38	K = 39.1
Br = 79.95	Kr = 81.8	Rb = 85.4
I = 127	Xe = 128	Cs = 132.9

The five well-known alkali metals correspond to the newly discovered argon analogues, and the atomic weights of both exhibit the same common law of periodicity. But the halogens and alkali metals are the most chemically active among the elements, and are, moreover, of opposite chemical character, the first being particularly prone to react with metals and the others with metalloids, the former appearing at the anode and the latter at the cathode. They must therefore stand at the two extremes of the periodic system, as in the scheme on p. 518.

Although this arrangement best expresses the periodic law, the distribution of the elements according to groups and series in the table on page 519 is perhaps clearer.

—		Higher saline oxides	Groups	Large periods, Elements of even series										—
Distribution of the Elements in Periods				I	R ₂ O	K = 39.1	Rb = 85.4	Cs = 132.9	—	Rd = 224				
				II	RO	Ca = 40.1	Sr = 87.6	Ba = 137.4	—	Th = 232				
				III	R ₂ O ₃	Sc = 44.1	Y = 89.0	La = 139	Yb = 173	U = 239				
				IV	RO ₂	Ti = 48.1	Zr = 90.6	Ce = 140	—	—				
				V	R ₂ O ₅	V = 51.4	Nb = 94.0	—	Ta = 183	—				
				VI	RO ₃	Cr = 52.1	Mo = 96.0	—	W = 184	—				
				VII	R ₂ O ₇	Mn = 55.0	? = 99.4	—	—	—				
				VIII		Fe = 55.9	Ru = 101.7	—	Os = 191	—				
						Co = 59	Rh = 103.0	—	Ir = 193	—				
				Ni = 59	Pd = 106.5	—	Pt = 194.9	—	—					
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Series	Zero Group	Group I	Group II	Group III	Group IV	Group V	Group VI	Group VII	
0	<i>x</i>								
1		Hydrogen H = 1.008							
2	Helium He = 4.0	Lithium Li = 7.03	Beryllium Be = 9.1	Boron B = 11.0	Carbon C = 12.0	Nitrogen N = 14.04	Oxygen O = 16.00	Fluorine F = 19.0	Group VIII Iron Fe = 55.9 Cobalt Co = 59 Nickel Ni = 59 (Cu)
3	Neon Ne = 19.9	Sodium Na = 23.05	Magnesium Mg = 24.1	Aluminium Al = 27.0	Silicon Si = 28.4	Phosphorus P = 31.0	Sulphur S = 32.06	Chlorine Cl = 35.45	
4	Argon Ar = 38	Potassium K = 39.1	Calcium Ca = 40.1	Scandium Sc = 44.1	Titanium Ti = 48.1	Vanadium V = 51.4	Chromium Cr = 52.1	Manganese Mn = 55.0	
5		Copper Cu = 63.6	Zinc Zn = 65.4	Gallium Ga = 70.0	Germanium Ge = 72.3	Arsenic As = 75.0	Selenium Se = 79	Bromine Br = 79.95	
6	Krypton Kr = 81.8	Rubidium Rb = 85.4	Strontium Sr = 87.6	Yttrium Y = 89.0	Zirconium Zr = 90.6	Niobium Nb = 94.0	Molybdenum Mo = 96.0		Ruthenium Ru = 101.7 Rhodium Rh = 103.0 Palladium Pd = 106.5 (Ag)
7		Silver Ag = 107.9	Cadmium Cd = 112.4	Indium In = 114.0	Tin Sn = 119.0	Antimony Sb = 120.0	Tellurium Te = 127	Iodine I = 127	
8	Xenon Xe = 128	Cæsium Cs = 132.9	Barium Ba = 137.4	Lanthanum La = 139	Cerium Ce = 140				(—)
9									
10				Ytterbium Yb = 173		Tantalum Ta = 183	Tungsten W = 184		Osmium Os = 191 Iridium Ir = 193 Platinum Pt = 194.9 (Au)
11		Gold Au = 197.2	Mercury Hg = 200.0	Thallium Tl = 204.1	Lead Pb = 206.9	Bismuth Bi = 208			
12			Radium Rd = 224		Thorium Th = 232		Uranium U = 239		

Here x and y stand for two unknown elements having atomic weights less than that of hydrogen, whose discovery I now look for.

A reference to the above remarks on the argon group of elements shows first of all that such a zero group as they correspond to could not possibly have been foreseen under the conditions of chemical knowledge at the time of the discovery of the periodic law in 1869; and, although I had a vague notion that hydrogen might be preceded by some elements of less atomic weights, I dared not put forward such a proposal, because it was purely conjectural, and I feared to injure the first impression of the periodic law by its introduction. Moreover, in those days the question of the ether did not awaken much interest, for electrical phenomena were not then ascribed to its agency, and it is this that now gives such importance to the ether. But at the present time, when there can be no doubt that the hydrogen group is preceded by the zero group composed of elements of less atomic weights, it seems to me impossible to deny the existence of elements lighter than hydrogen.

Let us first consider the element in the first series of the zero group. It is designated by y . It will evidently exhibit all the fundamental properties of the argon gases. But first we must have an approximate idea of its atomic weight. To do this, let us consider the ratio of the atomic weights of two elements belonging to the same group of neighbouring series. Starting with $Ce = 140$ and $Sn = 119$ (here the ratio is 1.18), this ratio, in passing to the lower groups and series, increases constantly and fairly uniformly as the atomic weights of the elements under comparison decrease. But we shall limit our calculation to the first and second series, starting with $Cl = 35.45$; for (1) we are exclusively concerned with the lightest elements, (2) the ratio of the atomic weights is more accurate for these elements, and (3) the small periods of the typical elements (which should include the elements lighter than hydrogen) terminate with chlorine. As the atomic weight of chlorine is 35.45, and that of fluorine 19.0, the ratio $Cl : F = 35.4 : 19.0 = 1.86$; so also we find:

Group VII	Cl	:	F	= 1.86
VI	S	:	O	= 2.00
V	P	:	N	= 2.21
IV	Si	:	C	= 2.37
III	Al	:	B	= 2.45
II	Mg	:	Be	= 2.67
I	Na	:	Li	= 3.28
0	Ne	:	He	= 4.98

This proves that the ratio in the given series distinctly and progressively increases in passing from the higher to the lower groups; and, moreover, that it varies most rapidly between the first and zero groups. It follows therefore that the ratio $He : y$ will be considerably greater than the ratio $Li : H$, which is 6.97, so that the ratio $He : y$ will be at least 10 and probably even greater. Hence, as the atomic weight $He = 4.0$, the atomic weight of y will be not greater than $\frac{4.0}{10} = 0.4$ and probably less. Such an analogue of helium may perhaps be found in eoronium, whose spectrum,

clearly visible in the solar corona above (that is, further from the sun than) that of hydrogen, is simple like that of helium, which seems to indicate that it belongs to a gas resembling helium, which was also predicted from its spectrum by Lockyer. Young and Harkness independently observed the spectrum of this unknown element during the solar eclipse of 1869. It is characterised by a bright-green line of wavelength $531.7\mu\mu$, while helium is characterised by a yellow line, $587\mu\mu$. Nasini, Anderlini, and Salvadori think that they discovered traces of coronium in their observations on the spectra of volcanic gases (1893). And as the lines of coronium were also observed, even at distances many times the radius of the sun above its atmosphere and protuberances, where the hydrogen lines are no longer visible, it is evident that coronium should have a less density and atomic weight than hydrogen. Moreover, as the ratio of the specific heats (at a constant pressure and for a constant volume) of helium, argon, and their analogues gives reason for thinking that their molecules (i.e., the amount of matter occupying, according to Avogadro-Gerhardt's law, a volume equal to the volume of two parts by weight of hydrogen) contain only one atom (like mercury, cadmium, and most metals), it follows that, if 0.4 be the greatest atomic weight of the element y , its density referred to hydrogen should be less than 0.2. Consequently the molecules of this gas will, according to the kinetic theory of gases, move 2.24 times faster than those of hydrogen, and if, as Stoney (1894-1898) and Rostovsky (1899) endeavour to prove, the progressive motion of the molecules of hydrogen and helium be such that they can leap out of the sphere of the earth's attraction, then a gas whose density is at least five times less than that of hydrogen could certainly only exist in the atmosphere of a body having as great a mass as the sun.

However, this y —coronium or some other gas with a density about 0.2—cannot possibly be ether, its density being too great. It wanders, perhaps for ages, in the regions of space, breaks from the shackles of the earth, and again comes within its sphere, but still it cannot escape from the regions of the sun's attraction, and there are many heavenly bodies of greater mass than the sun. But the atoms of ether must be of another kind; they must be capable of overcoming even the sun's attraction, of freely permeating all space, and of penetrating everything and everywhere. The element y , however, is necessary for us to be able to mentally realise the lightest and therefore swiftest element x , which I consider may be looked upon as the ether.

We have seen that, besides the ordinary groups of the chemically active elements, a zero group of chemically inactive elements must now be recognised for helium, argon, and their analogues. Thanks to Ramsay's exemplary researches, these elements are now tangible realities, authentic gases foreign to chemical association, that is, distinguished by their specific property of not being chemically attracted to each other or to other atoms even at infinitely small distances, and yet having weight, that is, subject to the laws of attraction of mechanics, which has nothing in common with chemical attraction. There is some hope that gravity may in some way or another be explained by means of pressure or impact acting from all sides, but chemical

attraction, which only acts at infinitely small distances, will long remain an incomprehensible problem. The problem of the ether is more or less closely connected with that of gravity, and gains in simplicity when all question of the chemical attraction of the atoms of ether is excluded, and this is accomplished by placing it in the zero group. But if the series of the elements begins with series I containing hydrogen, the zero group has no place for an element lighter than γ , like ether. I therefore add a zero series, besides a zero group, to the periodic system, and place the element x in this zero series, regarding it (1) as the lightest of all the elements both in density and atomic weight; (2) as the most mobile gas; (3) as the element least prone to enter into combination with other atoms; and (4) as an all-permeating and penetrating substance. Of course, this is an hypothesis, but it is one constructed not for purely 'working' ends, but simply from a desire to extend the real periodic system of the known elements to the confines or limits of the lowest dimensions of atoms, which I cannot and will not regard in the light of a simple nullity called mass.

Being unable to conceive the formation of the known elements from hydrogen, I can neither regard them as being formed from the element x , although it is the lightest of all the elements. I cannot admit this, not only because no fact points to the possibility of the transformation of one element into another, but chiefly because I do not see that such an admission would in any way facilitate or simplify our understanding of the substances and phenomena of nature. And when I am told that the doctrine of unity in the material of which the elements are built up responds to an aspiration for unity in all things, I can only reply that at the root of all things a distinction must be made between matter, force, and mind; that it is simpler to admit the germs of individuality in the material elements than elsewhere; and that no general relation is possible between things unless they have some individual character resident in them. In a word, I see no object in following the doctrine of the unity of matter, while I clearly see the necessity of recognising the unity of the substance of the ether and of realising a conception of it, as the uttermost limit of that process by which all the other atoms of the elements were formed, and by which all substances were formed from these atoms. To me this kind of unity is far more real than any conception of the formation of the elements from a single primary matter. Neither gravity nor any of the problems of energy can be rightly understood without a real conception of the ether as a universal medium transmitting energy at a distance. Moreover, a real conception of ether cannot be obtained without recognising its chemical nature as an elementary substance, and in these days no elementary substance is conceivable which is not subject to the periodic law.

I shall therefore, in conclusion, endeavour to show what consequences should follow from the above conception of the ether, from an experimental or realistic point of view, even should it never be possible to isolate or combine or in any way grasp this substance.

Although it was possible to approximately determine the atomic weight of the element γ on the basis of that of helium, this cannot be repeated for the element x , because it lies at the frontier or limit, about the zero point of

the atomic weights. Moreover, the analogues of helium cannot serve as a basis owing to the uncertainty of their numerical data. However, if the ratio of the atomic weights be $\text{Xe} : \text{Kr} = 1.56 : 1$; $\text{Kr} : \text{Ar} = 2.15 : 1$; and $\text{Ar} : \text{He} = 9.5 : 1$, we find that $\text{He} : x = 23.6 : 1$; or if $\text{He} = 4.0$, that the atomic weight of $x = 0.17$. This must be considered the maximum possible value. Most probably the atomic weight of x is far less, for the following reasons. If the gas in question be an analogue of helium, its molecule will contain one atom, and therefore its density, referred to that of hydrogen, must be about half its atomic weight or $\frac{x}{2}$, where x is the atomic weight. In

order to be able to permeate throughout all space, its density must be so small, compared with that of hydrogen, that its molecular motion would allow it to overcome the attraction, not only of the earth and sun, but also of all the stars, as otherwise it would accumulate about the largest mass and not fill all space. The velocity of the molecular motion of a gas by which the gaseous pressure is determined—by the number of impinging particles and their *vis viva*—is calculated, according to the kinetic theory of gases, by an expression containing a constant divided by the square root of the density of the gas and multiplied by the square root of $(1 + at)$ which expresses the expansion of the gas by heat. In the case of hydrogen (density = 1) at $t = 0^\circ$, the mean velocity of the particles, calculated on the basis that a litre of hydrogen at 0° and 760 mm. weighs about 0.09 gm., is 1843 metres a second, that of oxygen being 461 metres, for its density is 16 times that of hydrogen, i.e., $v = \frac{1843}{4} = 461$. Thus the velocity increases as the density

becomes less and as the temperature becomes greater, but does not depend upon the number of molecules in a given volume; and if our gas have an atomic weight x and density (referred to hydrogen) $\frac{x}{2}$, then the velocity of its molecules will be :

$$v = 1843 \sqrt{\frac{2(1 + at)}{x}} \quad . \quad . \quad . \quad . \quad . \quad (I)$$

In this expression x is the unknown quantity, to find which we must know t and v , or the velocity required by the particles to escape from the sphere of the earth's, sun's, and stars' attraction, like the projectile in Jules Verne's 'Voyage to the Moon.'

As regards the temperature of space, this can only be regarded as the absolute zero by those who deny the material nature of the ether, for temperature in a perfect vacuum or in space devoid of matter is an absurdity, and a solid such as an *aërolite* or thermometer introduced into such space would alter the temperature, not by contact with the surrounding medium, but solely by radiation. But if space be filled with the substance of ether, it not only may, but must have its own temperature, which evidently cannot be absolute zero. Many methods have been tried to determine this temperature, but it is unnecessary to discuss them here. Suffice it to say that no one has found it less than -150° or above -40° ; as a rule, the limits are taken as -100° and -60° . It is hopeless to expect any definite or

exact data on this subject, and probably the temperature varies in different localities owing to radiation being different in different parts of space. Moreover, the value of t between -100° and -60° has hardly any significance in an approximate evaluation of x , as only the maximum value of x can be calculated by the expression (I); for there can be no question of any exact value, all that is required being to obtain an idea of the order in which x stands among the elements. We therefore take the mean temperature $t = -80^\circ$; then if $a = 0.000367$,

$$v = \frac{2191}{\sqrt{x}} \quad \text{or} \quad \frac{4800000}{v^2} \quad . \quad . \quad . \quad . \quad (II)$$

where x is the atomic weight of the gaseous element required referred to hydrogen, and v the velocity of motion of its particles at -80° in metres per second.

This velocity must now be determined. We know that a body thrown up in the air falls back to the earth, and in so doing describes a parabola. The height of its flight increases as its initial velocity is made greater, and it is evident that this velocity might be such that the body would pass beyond the sphere of the earth's attraction, and fall on some other heavenly body, or rotate about the earth as a satellite by virtue of the laws of gravitation. It has been calculated that to do this the velocity of the body must exceed the square root of double the mass of the attracting body divided by the distance from its centre of gravity to the point at which the velocity is to be determined. The mass of the earth is calculated in absolute units from the mean radius of the earth ($= 6,373,000$ metres) and the mean attraction of gravity at the surface of the earth ($= 9.807$ metres), for the attraction of gravity is equal to the mass divided by the square of the distance (in this instance, the square of the earth's radius), and therefore the mass of the earth $= 398.10^{12}$, and the velocity sought for must therefore exceed $11,190$ metres a second. Hence, according to formula (II), the atomic weight of such a gas must be less than 0.038 to enable it to escape freely from the earth's atmosphere into space. All gases of greater atomic weight, not only hydrogen and helium, but even the gas γ (coronium?), will remain in the earth's atmosphere.

The mass of the sun is approximately $325,000$, if that of the earth be taken as unity. Hence the absolute magnitude of the sun's mass will be nearly 129.10^{18} . The radius of the sun is 109.5 times greater than that of the earth, i.e., nearly 698.10^{16} metres. Hence only bodies or particles having a velocity of not less than $\sqrt{\frac{2.129.10^{18}}{698.10^{16}}}$ or about

$608,300$ metres a second, could escape from the surface of the sun. According to formula (II), the atomic weight of a gas x having such a velocity will not be greater than 0.000013 , and its density will be half this figure. Hence the atomic weight and density of such a gas, which, like the ether, permeates space, must at all events be less than this figure. This is inevitable because there are stars of greater mass than the sun. This has been proved by researches made on the double stars.

The most exact data we now possess concern Sirius, whose total mass including that of its satellites is 3.24 times that of the sun. To determine

this it was necessary to investigate not only the relative motion of both stars, but also the parallax of this system. In the case of Sirius it was possible to determine the ratio of the masses of the two stars. This was found to be 2.05; so that the mass of one star is 2.20, and that of the other 1.04, times that of the sun. In the following cases only the total mass of the two twin stars was determined relative to that of the sun:

α Centauri	2.0
70 Ophiuchi	1.6
μ Cassiopeiæ	0.52
61 Cygni	0.34
γ Leonis	5.8
γ Virginis	32.70

The mass of β Persei with its satellites is 0.67 time that of the sun, the mass of the star being twice that of its satellite. The triple star 40 Eridani has a mass 1.1 time that of the sun, the mass of the brightest star being 2.37 times that of the other two.

It appears, therefore, that although there are some stars which are greater, and some which are less, still the mass of the sun is nearly the average of that of the other stars. For our purpose we need only consider the stars of much greater mass than the sun. That of the double star γ Virginis has a common mass about 33 times that of the sun. There is no reason for thinking that this is the maximum, and it will therefore be safer to infer that there may be stars whose mass exceeds 50 times that of the sun; but I do not think it likely that a larger mass than this is in the nature of things. To complete our calculation it is also necessary to know the radius of the stars, about which we have no direct data. However, the composition and temperature of the stars may give a clue. Spectrum analysis proves that the terrestrial chemical elements occur in the most distant heavenly bodies, and from analogy there seems no doubt that the general mass composition of these bodies is very similar in all cases; that is to say, they are composed of a dense core surrounded by a less dense crust and an atmosphere which becomes gradually rarefied. Thus the composition of the stars probably differs but little from that of the sun, and the density is determined by the composition, temperature, and pressure. Only at the core can the density differ much from that of the sun, but this cannot greatly affect the average density. Neither can the temperature of the stars differ greatly from that of the sun. Moreover, a rise of temperature would tend to increase the diameter of the star, and this would decrease the value of the velocity required by the gaseous particles to escape from the sphere of attraction. It appears, therefore, that for the purposes of our calculation the average density of the large stars may be taken as nearly that of the sun, and therefore that the radius of a star whose mass is n times that of the sun will be $\sqrt[3]{n}$ times the radius of the sun. We now have all the data necessary for calculating the velocity required by gaseous particles to escape from the sphere of attraction of a star 50 times greater than the sun.

Its mass is $50.129.10^{16}$, or nearly 65.10^{20} , and its radius nearly $698.10^6 \sqrt[3]{50}$, or 26.10^8 . Hence the velocity required will be nearly :

$$\sqrt{\frac{2.65 \times 10^{20}}{26 \times 10^8}} = 2,240,000 \text{ metres per second, or } 2,240 \text{ kilometres per second.}$$

The great magnitude of this velocity, v , and its proximity to that of light (300,000,000 metres a second) provoke the following inquiry: How much must the mass of a heavenly body exceed that of the sun in order to retain on its surface particles endowed with a velocity of 3.10^8 metres per second, if its mean density were equal to that of the sun? This may be calculated from the fact that if the mean density of the two luminaries be equal, the velocities of bodies able to escape into space from the spheres of attraction will stand in the ratio of the cube roots of their masses, and therefore a luminary from whose surface particles endowed with a velocity of 300,000,000 metres per second could escape must have a mass 120,000,000 times that of the sun, for only particles having a velocity of 608,000 metres a second can escape from the sun, and this stands to 300,000,000 in the ratio 1 : 493, and the cube of 493 is nearly 120,000,000.

But, so far we have no reason for admitting the existence of such a huge body, and therefore it seems to me that the velocity of the particles of our gas (ether) must, in order to permeate space, be greater than 2,240,000 metres a second, and probably less than 300,000,000 metres a second.

Hence the atomic weight of x as the lightest elementary gas, permeating space and performing the part of the ether, must be within the limits (formula II) of 0.000,000,96 and 0.000,000,000,053, if that of H = 1.

I think it is impossible, under the present conditions of our scientific knowledge, to admit the latter value, because it would in some measure answer to a revival of the emission theory of light, and I consider that the majority of phenomena are sufficiently explained by the fact that *the particles and atoms of the lightest element x, capable of moving freely everywhere throughout the universe, have an atomic weight nearly one millionth that of hydrogen, and travel with a velocity of about 2,250 kilometres per second.*

When I was making these calculations my friend Professor Dewar sent me his presidential address to the Belfast meeting of the British Association. In it he expresses the thought that the highest regions of the atmosphere, which are the seat of the aurora borealis, must be considered to be the province of hydrogen and of the argon analogues. This is only a few steps from the yet more distant regions of space, and from the necessity of recognising the existence of a still lighter gas capable of permeating and filling space, and thus giving a tangible reality to the conception of the ether.

In conceiving of the ether as a gas endowed with the above properties and belonging to the zero group of elements, I desired before all to extract from the periodic law that which it was able to give and to tangibly explain the materiality and universal presence of an ethereal substance throughout nature, and also to explain its faculty of permeating all substances, gaseous, liquid, and solid. The atoms of even the lighter elements forming the ordinary substances being several million times heavier than those of ether, they are not likely to be greatly influenced in their mutual relations by its presence.

Of course there are still many problems to be solved, but I think the majority are unfathomable, and I have no intention of raising them here or of trying to solve those which appear capable of being solved. My only purpose has been to state my opinion on a subject about which I know many are thinking and some are beginning to speak.

Without going into a further development of our subject, I should like to acquaint the reader with some, at first sight, auxiliary circumstances which guided my thoughts and led me to publish my opinions. These consist of a series of recently discovered physico-chemical phenomena which are not subject to the ordinary doctrines of science, and have caused many to return to the emission theory of light, or to accept the, to me, vague hypothesis of electrons, without trying to explain to the utmost the familiar conception of an ethereal medium transmitting luminous vibrations, &c. This more especially refers to radio-active phenomena.

I need not describe these most remarkable phenomena, assuming that the reader is more or less acquainted with them, and shall only mention that a perusal of the literature of the subject, and what I saw in M. Becquerel's laboratory and heard from him and M. and Madame Curie, gave me the impression of some peculiar state proper chiefly (but not exclusively, just as magnetism is chiefly, but not exclusively, the property of iron and cobalt) to uranium and the thorium compounds.

As uranium and thorium, and also radium, judging from Madame Curie's researches (1902), have the highest atomic weights ($U = 239$, $Th = 232$, and $Rd = 224$) among the elements, they may be looked upon as suns, endowed with the highest degree of that individualised attractive capacity, a mean between gravity and chemical affinity, which is seen in the absorption of gases, solution, &c. By conceiving the substance of the ether as the lightest of gases, x , deprived, like helium and argon, of the power to form stable definite compounds, it need not be imagined that this gas is deprived of the faculty of, as it were, dissolving in or accumulating about large centres of attraction like the sun among heavenly bodies, or uranium and thorium in the world of atoms. As a matter of fact, direct experiment proves that helium and argon are able to dissolve in liquids, and, moreover, to individualise this faculty according to either their own nature or that of the liquid and according to the temperature. If the ether is a gas, x , it must naturally accumulate from all parts of the universe towards the medium or mass of the sun, just as the gases of the atmosphere accumulate in a drop of water. And the lightest of gases, x , will also accumulate about the heaviest atoms of uranium and thorium, and perhaps change its form of motion like a gas dissolved in a liquid. This will not be a definite act of combination, determined by a conformable harmonious motion, like the motion of a planet and its satellites, but an embryo of such a motion, resembling that of a comet in the region of heavenly individualisations, and it may be looked for sooner in the region of the heaviest atoms of uranium and thorium than in those of the lighter elements, just as a comet falling from space into the planetary system revolves round the sun and then once more escapes into space. If such a special accumulation of ether atoms about the molecules of uranium and thorium be admissible, they might be expected to exhibit

peculiar phenomena, determined by the emission of a portion of this ether held by particles of normal mean velocity and by new ether entering into the sphere of attraction. It seems to me that the optical and photo-radiant phenomena, not to mention the loss of electrical charges, indicate a material flow of something which has not been weighed, and it appears to me that they might be understood in this manner, for peculiar forms of the entrance and egress of ether atoms should be accompanied by such disturbances in the ethereal medium as give the phenomena of light. M. and Madame Curie showed me the following experiment, for instance. Two small flasks were connected together by a lateral tube fused into their necks, and having a stopcock in the middle. The cock being closed, a solution of the radio-active substance was poured into one of the flasks, while a gelatinous white precipitate of sulphide of zinc, shaken up in water, was placed in the other flask. Then both flasks were closed. So long as the cock between the flasks remains closed, nothing is visible in the dark; but directly it is opened, the sulphide of zinc becomes brilliantly fluorescent and continues so as long as the tube connecting the flasks remains open. This experiment gives the impression of an emissive flow of something material from the radio-active substance, and, in a sense, seems comprehensible if we assume that a peculiar rarefied ether gas, capable of exciting luminous vibrations, enters and passes off from the radio-active substance. Just as any kind of motion may be set up in a gas, not only by a solid piston, but also by the motion of another portion of the same gas, so also the phenomenon of light, i.e., a certain transverse vibration of ether, may be produced not only by the molecular motion of particles of other bodies (by heating them or otherwise) bringing the ether from its state of mobile equilibrium, but also by a certain change in the motion of the ether atoms themselves; i.e., by their destroying their own equilibrium which may be caused in the case of the radio-active bodies by the massiveness of the atoms of uranium and thorium, just as the luminosity of the sun may be, I think, due to its great mass being able to accumulate ether in far larger quantities than the planets, &c. I think that the radio-luminous phenomena, i.e., such as proceed at right angles to the ray of the vibration of the ether medium, consisting of minute atoms in rapid motion, are, as a matter of fact, more complex than has hitherto been thought, chiefly owing to the fact that the velocity of the ether atoms is not very much less (130 times) than that of the propagation of their transverse vibrations. This at all events was the impression I acquired from the radio-active phenomena I saw, and I do not conceal it, although I consider it very difficult to form any opinion on this still dim province of the phenomena of light.

In conclusion, I may mention another class of phenomena, which led me to this conception of the ether. Dewar, about 1894, in his researches on the phenomena proceeding at low temperatures, observed that the phosphorescence of many substances, and especially of paraffin, becomes more intense at the temperature of liquid air (between -181° and -193°). Now, it appears to me that this is due to the fact that paraffin and such like substances have a great capacity for condensing the atoms of ether at very low temperatures. In other words that the solubility (absorption) of the ether in some

bodies increases in extreme cold. They therefore become more phosphorescent, for the vibrations of light are then set up in the phosphorescent substances, not only by their own atoms (having the property of illumination at their surface, of passing into a state of peculiar tension, which causes, when the act of illumination ceases, the ether to vibrate), but also by the atoms of ether which condense in these bodies and set up a rapid state of interchange with the surrounding medium.

It seems to me that this conception of ether, as a peculiar all-permeating gas, gives a means, if not of analysing such phenomena, at all events of understanding their possibility. I do not regard my imperfect endeavour to explain the nature of ether from a chemical point of view as more than the expression of a series of thoughts which have arisen in my mind, and which I have given vent to solely from a desire that these thoughts, being suggested by facts, should not be utterly lost. Most probably similar thoughts have come to many, but unless they are enunciated they often pass away without being further developed. If they contain a particle of that natural truth which we all seek, my effort will not have been in vain; it may then be worked out, embodied, and corrected, and if my conception be proved false in its basis, it will prevent others from repeating it. I know of no other way for slow and steady progress. And even if it be found impossible to recognise in the ether the properties of the lightest, most mobile, and chemically inactive gas, still, if we keep to the realism of science, we cannot deny its substantiality, and this requires a search for its chemical nature. My effort is no more than a tentative answer to this primary question, and its one object is to bring this question to the fore.

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